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# ACUTE LETHALITY AND RELATED CONTAMINANTS IN THE RAINY RIVER DOWNSTREAM OF TWO BOISE CASCADE KRAFT MILL DISCHARGES

AUGUST 1989

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# ACUTE LETHALITY AND RELATED CONTAMINANTS IN THE RAINY RIVER DOWNSTREAM OF TWO BOISE CASCADE KRAFT MILL DISCHARGES

Report prepared by:

K. Flood[1], A. Smith[2], D. Hollinger[3]
and M. Mueller[1,4]

1. Bioassessment Unit, Aquatic Biology Section, Water Resources Branch, Rexdale.
2. Biology Department, Lakehead University, Thunder Bay.
3. Water Resources Assessment Unit, Technical Support Section, Northwestern Region, Thunder Bay.
4. Present Address: Toxicity Unit, Aquatic Biology Section, Water Resources Branch.

AUGUST 1989

HAZARDOUS CONTAMINANTS
COORDINATION BRANCH
135 ST. CLAIR AVENUE WEST
TORONTO, ONTARIO M4V 1P5

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# SUMMARY

In recent years, the two Boise Cascade pulp mills, located on the Rainy River in Fort Frances and International Falls, have undertaken several significant pollution abatement measures to improve the quality of their effluents. The International Rainy River Water Quality Board recommended a major study to assess the effects of those improvements on the water quality of the river since the last major study in 1970. This study was undertaken as a result of a proposal by the Board to include _in situ_ bioassay testing in the river to measure acute lethality using caged fish, as part of that assessment.

Laboratory bioassays were performed on both mill effluents during the study. The International Falls mill effluent was non-lethal while the effluent from the Fort Frances mill produced an LC50 which ranged from 29% to 43%. In all four tests, the Fort Frances mill effluent failed the Ontario Government toxicity test requirement for pulp mill effluents, of at least 50% rainbow trout survival in a 100% effluent concentration. These findings are representative of toxicity results normally produced by both mill effluents in 1986.

The effluent plume downstream of the International Falls mill was not acutely lethal to fish, and lethality downstream of the Fort Frances mill did not occur at significant levels relative to control mortality. Therefore, acute lethality to fish immediately downstream of both Boise Cascade pulp mills is not considered to be a problem under normal mill operations and low flow river conditions.

Elevated chlorophenol residues in fish occurred in two main areas of the river immediately downstream of Fort Frances and International Falls. Levels of 2,4,6-trichlorophenol (2,4,6-TCP) were detected in fish caged at the diffuser upwelling of the Fort Frances mill and pentachlorophenol (PCP) was found in fish caged downstream of the International Falls town STP. The chlorophenol levels found in those fish are considered as very low relative to expected values downstream of bleached kraft mill effluents.

The maximum 2,4,6-TCP and PCP levels in water samples from the Rainy River downstream of the mills were 690 ng/L and 100 ng/L, respectively. These levels are far below the current Provincial Water Quality Objectives of 18,000 ng/L for 2,4,6-TCP and 500 ng/L for PCP.

Therefore, based on levels in fish, river water and current sublethal results for chlorophenol studies presented in the literature, it is concluded that chlorophenol bioconcentration by fish under normal mill operating conditions at both Boise Cascade pulp mills is not considered to be a concern to fish health in the Rainy River.

Two dioxin and three furan congeners were detected in the Boise Cascade (Fort Frances) mill effluent and one dioxin congener was detected in the Boise Cascade (International Falls) mill effluent. These results are preliminary and lower detection levels would be required to fully define dioxin and furan contamination in these effluents on a qualitative and quantitative basis.

# INTRODUCTION

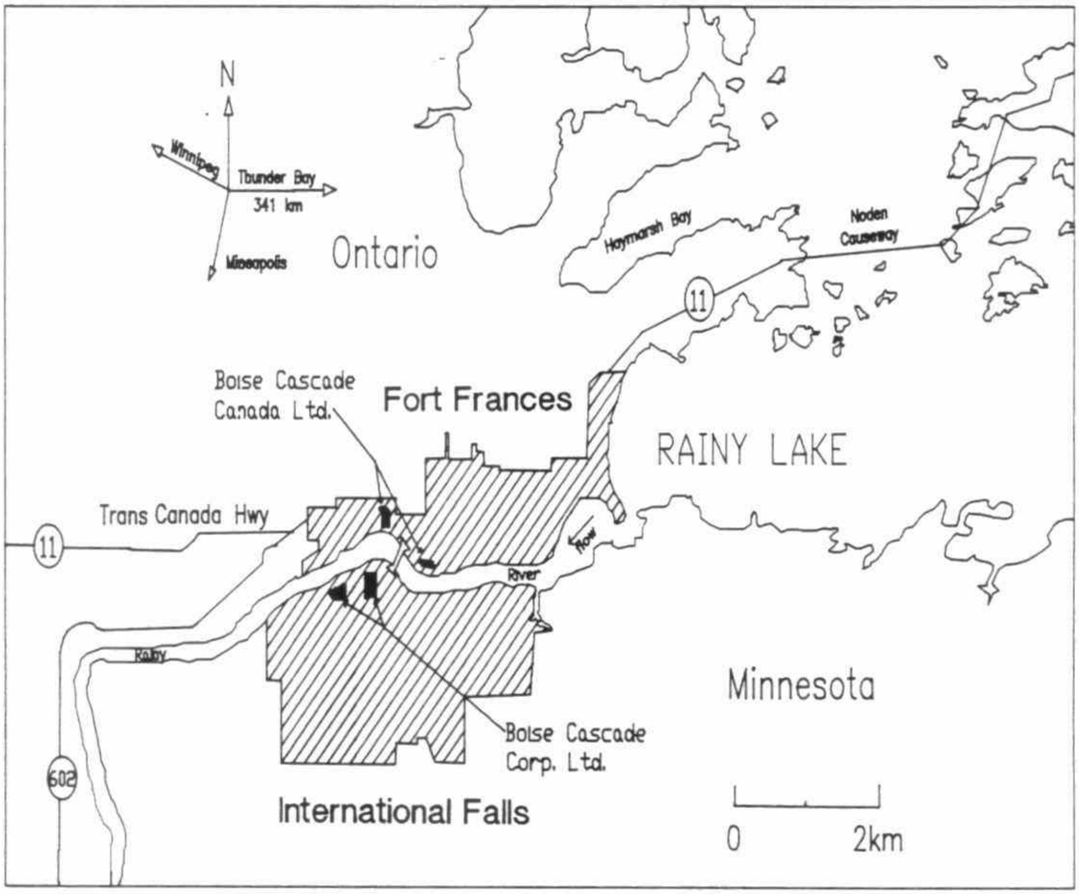
This report presents an assessment of the acute effects of effluents from two Boise Cascade pulp mills on fish caged in the Rainy River. The study was carried out as a result of a proposal by the International Rainy River Water Quality Board and was conducted in August, 1986. It was undertaken in conjunction with a Rainy River Contaminants Study, co-ordinated by the Northwestern Region of the Ontario Ministry of the Environment, and involving other participants from the Bioassessment Unit of the Water Resources Branch and from Environment Canada.

The objectives of this study were:

1. to evaluate the acute lethality of the mill discharges using laboratory bioassays and to identify the active ingredients in those samples which were lethal.
2. to determine the extent of fish lethality in the Rainy River downstream of the two pulp mills.
3. to compare laboratory and field bioassay results.
4. to measure chlorophenol levels in the river downstream of the two mills and related chlorophenol bioconcentration by caged fish.
5. to measure dioxin levels in the two mill effluents as part of the Rainy River Contaminants Study.

The two Boise Cascade mills are located on the Rainy River, 5 km downstream of Rainy Lake, and immediately downstream of the power dam and International Bridge which link Fort Frances, Ontario to International Falls, Minnesota (Figure 1). The Rainy River has a relatively uniform flow and width throughout its length. The average flow in the summer is approximately 250 cms, while low flow conditions of 70 cms were maintained during this study. The study area under the influence of the two mills encompassed approximately 8 km. The degree

Figure 1: Study Area in Rainy Lake and the Upper Rainy River



of mixing of the two effluents along the river centreline was predicted to be 90% at a 5 km distance downstream of the mills and 100%, 10 km downstream (Walker, prel. rep.). Complete lateral homogenity of the effluents across the entire river occurs at a very long distance downstream (Walker, prel. rep.).

Boise Cascade Canada Ltd. operates a bleached kraft and groundwood paper mill along the north shore of the river in the town of Fort Frances. Mill capacity approaches 1200 tonnes of product per day of which 500 tonnes is from the kraft mill. The process feedstock is essentially softwoods in the form of black spruce, jack pine and balsam fir logs and chips. Treatment of the effluent involves the removal of solids from the groundwood effluent by a clarifier, while the total mill effluent is treated biologically in an aerated lagoon, with further solids removal in a settling basin. From the foam chamber, the effluent is discharged to the Rainy River by way of a diffuser system located on the river bottom at a depth of 10m. The point of discharge is approximately 30 m offshore and at a point 75 m downstream of the generator discharge from the power dam; and hence, vertical dispersion of the effluent due to water turbulence occurs rapidly.

The final effluent of the Fort Frances mills was sampled eight times during 1986 and tested in nine 96-h standard laboratory bioassays for lethality using rainbow trout. The 96-h LC50 values from those nine tests ranged from 10% to 42.8% (OME, 1987).

Previous data for the Boise Cascade Fort Frances mill indicates the presence of chlorophenols in the final effluent (Cherwinsky & Murray, 1986). The analyses of fish in the Rainy River for chlorophenols were not undertaken in the OME Sport Fish or Young Fish Contaminants Program prior to 1986.

The other Boise Cascade mill which discharges into the Rainy River is located on the south shore of the river in the town of International Falls, Minnesota. It is an integrated bleached kraft mill which produces approximately 585 tonnes of fine paper products per day, using essentially a 70/30 mix of hardwoods (popular) to softwoods (pine & spruce), respectively (Al Meadows, pers. comm.). The effluent treatment system involves initial solids removal in a primary clarifier, and secondary treatment in a Unox oxygen-activated aeration basin (i.e. a high rate bio-treatment) with an associated secondary clarifier. The average volume of process wastewater treated per day in 1986 was 87,000 $m^3$, while a total mill effluent volume of 130,000 $m^3$/day (43.3 M gal. (U.S.)/day), including untreated cooling water, was discharged to the river through a multi-port diffuser system (Al Meadows, pers. comm.). Under low flow conditions, similar to those during this study, the effluent is discharged from the diffuser at the water surface.

In a 1985 report by the Minnesota Pollution Control Agency, duplicate 96-h flow through bioassays were undertaken to measure the acute lethality of the Boise Cascade (International Falls) mill effluent to fathead minnows. Reference was made to the fish being under stress immediately after introduction into the 75% and 100% test solutions of both bioassays; however, the effluent was found to be essentially non lethal after 96-h (i.e. non lethal in one bioassay and 5% mortality in 100% effluent for the replicate).

# METHODS

## 1. Study Outline

Preliminary lab bioassays were performed at Lakehead University in Thunder Bay and the OME Rexdale lab, during May, 1986. They were undertaken to compare the sensitivity of rainbow trout and brown trout to the two Boise Cascade mill effluents and an important pulp mill toxicant, abietic acid. This work was performed to determine whether an application factor would be required in order to compare the toxic response of brown trout in the field with that of rainbow trout used in concurrently-run lab bioassays. Brown trout were used in this *in situ* lethality study rather than rainbow trout, because of the greater tolerance of brown trout to water temperatures in excess of 20°C during an August exposure.

Hatchery-reared brown trout and lab-reared fathead minnows were exposed in Rainy Lake, and the Rainy River upstream and downstream of the two pulp mills from August 24-28, 1986. Daily observation of fish mortality and sampling for water chemistry were undertaken at each exposure site.

A concurrent program was carried out at Lakehead University which involved 96-h lab bioassays on daily samples of the two mill effluents using rainbow trout. Samples of those effluents were also submitted to the OME Rexdale lab for chemical analyses. Upon completion of the study, fish surviving the 96-hour *in situ* exposure were sacrificed and preserved for chlorophenol analyses.

## 2. Field Exposure

### (a) Test Fish

The brown trout (*Salmo trutta*) and fathead minnows (*Pimephales promelas*) were acclimated at Lakehead University, Thunder Bay, to a water temperature of 19°C and soft water conditions (hardness: 50 mg/L as $CaCO_3$) for 39 days prior to the exposure (further details available in Appendix A). The fish were placed in sealed food grade polyethylene bags, which contained 20 L of water and a 20 L oxygen headspace, and shipped to the test site in insulated coolers. The time from bagging to exposure of the fish involved approximately a 6-hour time period during which the fish were transported to the test sites by truck, plane and boat. Water temperatures at the exposure sites were within 1°C of the transport water and therefore the fish were immediately placed in the appropriate cages. Separate cages were used for each species when both were exposed at the same site.

(b) Fish Cages

The cages used in this study were constructed with a 1.9 cm (¾") polyvinylchloride (PVC) pipe frame with a triangular shape, top and bottom, and had three sides, each 0.5 m in length and depth. The frame supported a 0.6 cm(¼") mesh nylon bag with a draw string closure at the top.

The cages were free-floating with the cage top at the water surface and were held in place by a rope and anchor. An empty plastic container was also tied to the cages as a navigational marker.

(c) Cage Locations

Surveillance work by R. Walker (prel. rep.) indicated that each effluent plume hugged its respective shoreline for the first 2 km distance downstream of the mills and that 90% mixing at the centreline of the river would occur at a distance of 5 km downstream. Therefore, a set of cages was located close to shore at progressive distances downstream of each mill for a distance of up to approximately 8 km.

Cages were located at the water surface based on the fact that the Boise Cascade (International Falls) diffuser ports were discharging at the surface under low flow conditions and the Fort Frances mill diffuser produced an effluent upwelling directly above its port system.

A cage was not sited at station 4 (directly in the discharge upwelling) until 48-h into the study, for the upwelling could not be located until the afternoon of study day 2. A corresponding control was located immediately downstream of the dam spillway, at the time that the station 4 exposure began on day 3. The three principal control sites were located upstream of the mills, in: (1) Rainy Lake at an unnamed island offshore of Gash Point (C-1), at (2) Pithers Point (C-2) and, (3) tied to a log boom at the closest river access upstream of the International Bridge (C-3), (Figure 2). The study sites are shown in Figures 3 and 4.

## (d) Procedure

The cages were sited in pre-selected locations on the day before the study commenced. On the following day (August 24), fish were placed in the appropriate cages with 25 fish in a brown trout cage and 40 fish in a fathead minnow cage. Brown trout were exposed at every test site, except for site F, where the cage was missing on day 1, and at site 4, for no acclimated trout were available on day 3. Fathead minnow exposures were limited to sites C-1, 4, 8 and F, principally for bioaccumulation purposes. The testing of fathead minnows at sites 4 and F were limited to 48-h and 72-h time periods respectively, due to logistical reasons.

Mortality checks were limited to once a day over the 96-h exposure. Dead fish were removed immediately upon observation and discarded. After the 96-h exposure, five sets of composite samples each containing five fish or more were selected from individual sites for analyses of chlorophenols. These fish were sacrificed, weighed as composites, wrapped in hexane-washed foil and frozen for preservation. A pre-exposure set of fish composites were also sampled at the Thunder Bay lab for chlorophenol analyses.

The study dates and corresponding time descriptions at the beginning and end of the study are as follows:

| Date | Time | Study Day | Exposure Time |
|---|---|---|---|
| August 24 | 1400-h | 1 | 0 hours |
| August 28 | 1400-h | 5 | 96 hours |

Figure 2: Control Sites in Rainy Lake and the Rainy River

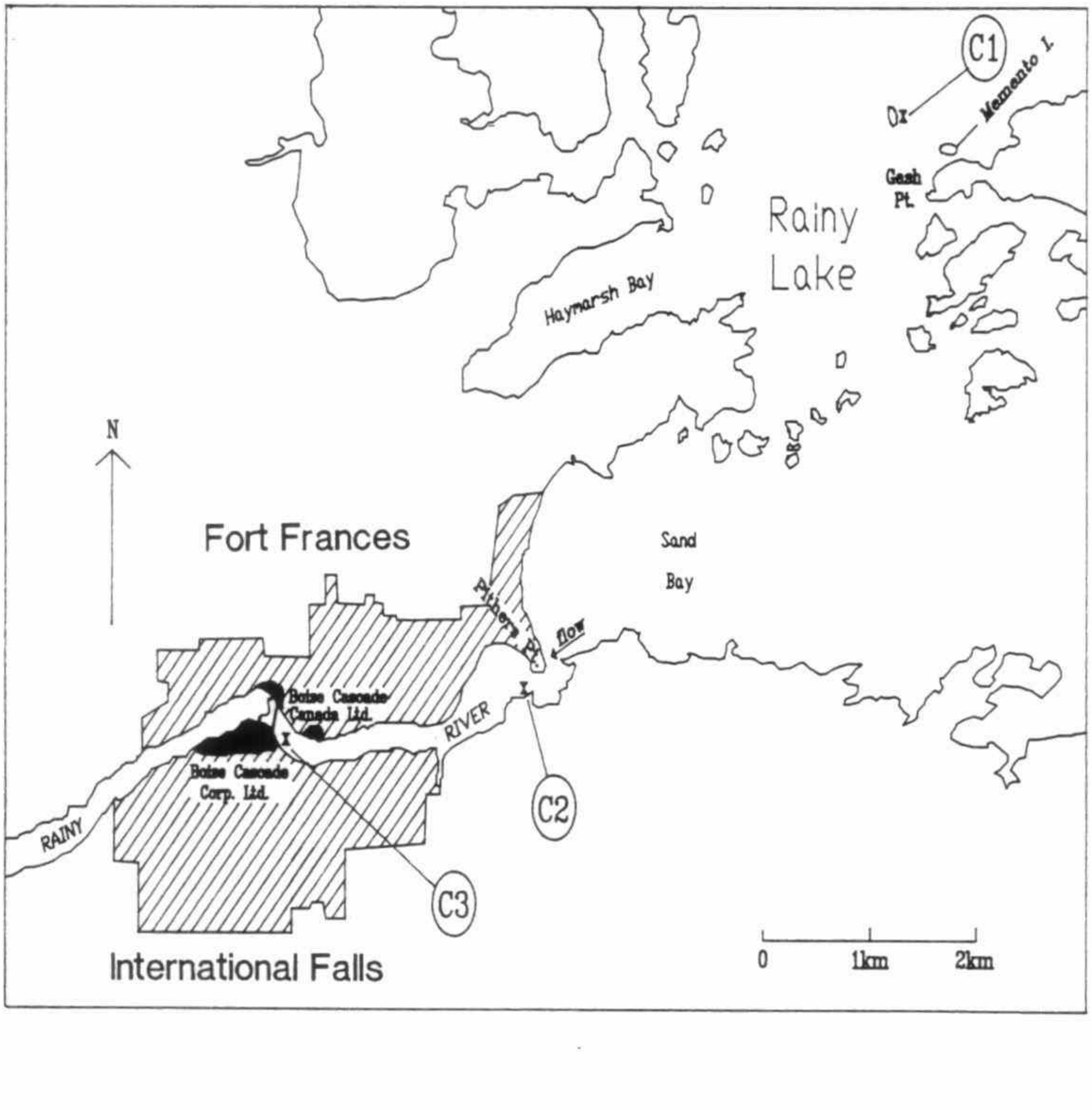


Figure 3: Fish Exposure Sites in the Vicinity of the Two Boise Cascade Mill Discharges.

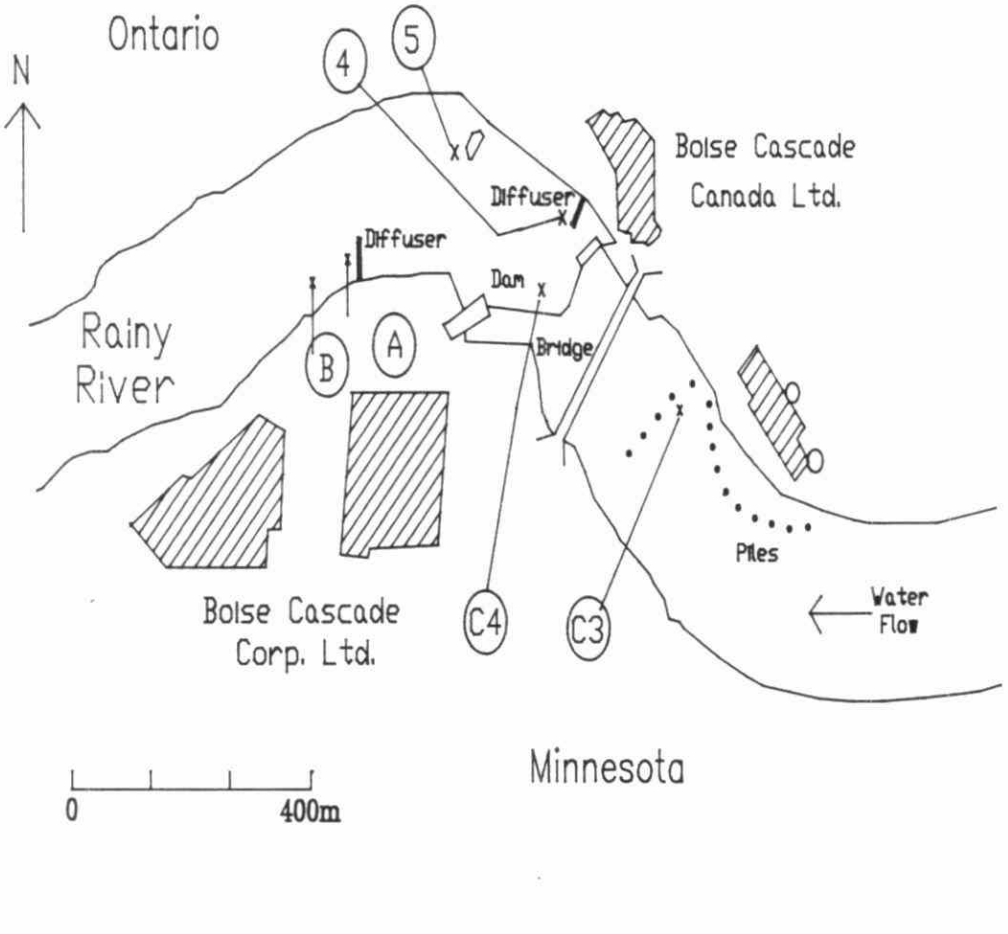
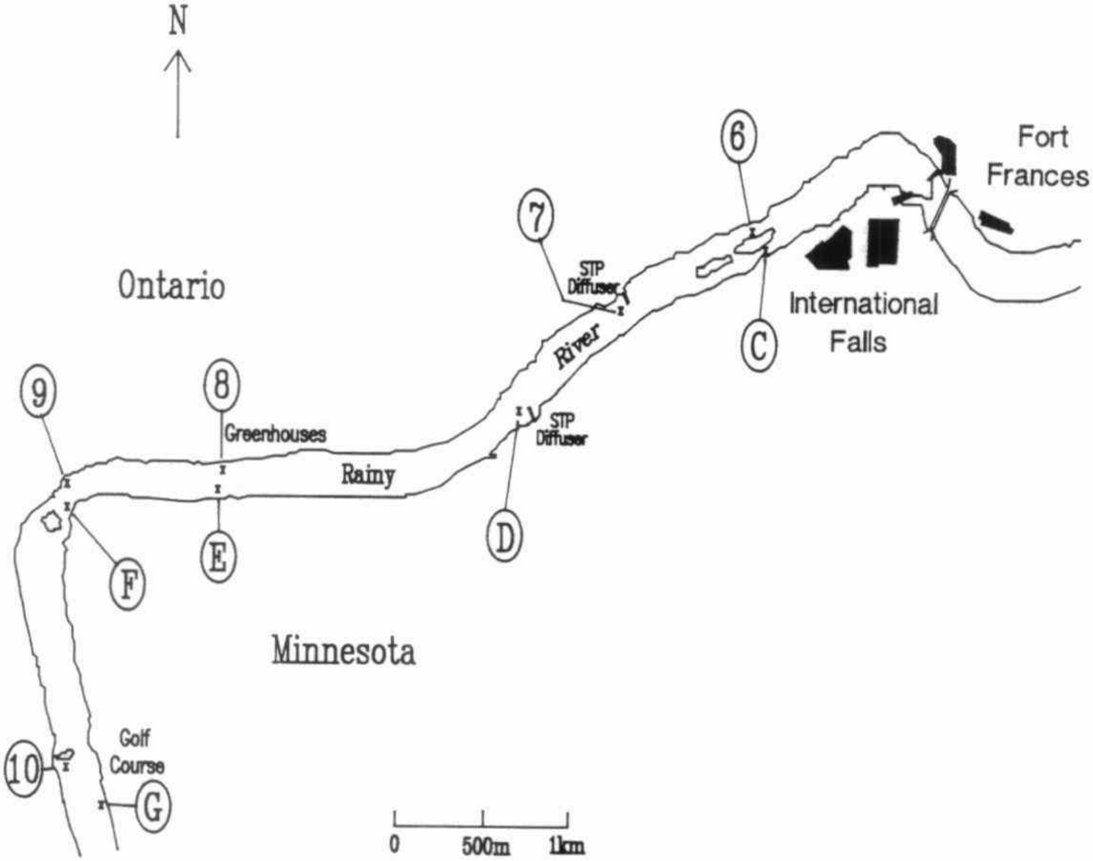


Figure 4: Fish Exposure Sites Downstream of the Two Boise Cascade Mill Discharges.



## 3. Physical and Chemical Analyses

### a) List of Analyses

i) total reactive phenolics;
ii) chlorophenols;
iii) phenoxy acids;
iv) resin and fatty acids;
v) organosulfur compounds;
vi) polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans;
vii) pesticides, PCBs, hexachlorobenzene and mirex;
viii) dissolved oxygen, conductivity, pH and temperature.

### b) Water Sampling Schedule

#### i) Effluent Samples

All pulp mill effluent samples were intended to be 24 h composites, collected from noon until noon on the dates listed below. When equipment malfunctions occurred, grab samples may have been substituted with collections occurring on the particular sampling dates listed below. The effluent sampling schedule was as follows:

| Boise Cascade Mill | Sample Purpose | Sample Type | Date | Study Day |
|---|---|---|---|---|
| Fort Frances | Chemistry | 24 h composite | Aug. 24-25 | 1-2 |
| | | | Aug. 25-26 | 2-3 |
| | | | Aug. 26-27 | 3-4 |
| | | | Aug. 27-28 | 4-5 |
| | Bioassays[1] | 24 h composite first 3 days[1] | | |
| | | 20 h composite | Aug. 27-28<br>(1600-1200 h) | 4-5 |

---

Note: [1] Composite samples were identical to those of the first three chemistry samples from the Fort Frances mill, listed above.

| Boise Cascade Mill | Sample Purpose | Sample Type | Date | Study Day |
|---|---|---|---|---|
| International Falls | Chemistry | 16 h composite | Aug. 24-25 (2100-1300 h) | 1-2 |
| | Chemistry | grab | Aug. 26 | 3 |
| | | 24 h composite | Aug. 26-27 | 3-4 |
| | | grab | Aug. 28 | 5 |
| | Bioassays | grab | Aug. 25 | 2 |
| | | grab | Aug. 26 | 3 |
| | | 24 h composite | Aug. 26-27 | 3-4 |
| | | grab | Aug. 28 | 5 |

The sewage treatment plant (STP) effluent collections from the towns of Fort Frances and International Falls were grab samples taken daily on study days 3-5 inclusive.

ii) River Water Samples

The river water samples were all collected as grab samples at the fish exposure sites between 1000-1300 h, on study days 1-5 inclusive.

c) Water Sampling Program

i) Effluent Samples

The two Boise Cascade mill effluents were sampled, as outlined in 3 b), for all scans and individual parameters listed in 3 a), except dissolved oxygen and temperature. The STP discharges were sampled for chlorophenols only.

ii) River Water Samples

- total reactive phenolics and chlorophenols were analyzed in grab samples from all sites downstream of the mills daily over the 96 h exposure.

- phenoxy acids - analyzed in grab samples from all sites downstream of the mills on days 3 & 4 of the study only.
- resin and fatty acids - analyzed in 3-daily grab samples collected during the first 48-h of a fish exposure at a particular site, for all sites downstream of the mills.
- organosulfides - analyzed in the 3 daily grab samples collected during the first 48-h of an exposure at a particular site, for all exposure sites downstream of the mills, to and including those at the two STP discharges.
- conductivity - single measurement daily at all sites downstream of the mills on study days 2-5 inclusive.
- dissolved oxygen, temperature and pH - single measurements daily at all sites downstream of the mill on study days 2, 3 & 4.

Test methodologies used in this study are contained in the "Handbook of Analytical Methods for Environmental Samples," compiled by the Ontario Ministry of the Environment, Laboratory Services Branch in December, 1983.

## 4. Laboratory Bioassays

Three sets of aerated 96-h bioassays were undertaken to measure acute lethality in the study. Two of the test sets were undertaken to compare the sensitivity of brown trout versus rainbow trout to the two Boise Cascade effluents and to a pulp and paper mill toxicant, abietic acid. The abietic acid bioassays were performed at the OME Rexdale lab in May, 1986. The test dilutions were prepared with dechlorinated Toronto tap water (hardness 130 mg/L as $CaC0_3$) and technical grade (85% pure) abietic acid, obtained from Aldridge Chemical, Milwaukee, Wisconsin. The Boise Cascade effluents were grab samples which were tested at Lakehead University in Thunder Bay during May 1986, using dechlorinated Thunder Bay tap water (hardness 50 mg/L as $CaCO_3$) for dilution purposes. The third set of bioassays were sampled as 24-h composite samples (or as described in Section 3 b) and tested at Lakehead University to measure the acute lethality of each mill effluent, over 5 days during the *in situ* fish exposure in August, 1986.

In each bioassay, 10 fish were exposed per test solution and sample concentrations ranged from 10 to 100% for the effluent samples and 1 to 10 mg/L for the abietic acid bioassays. Fish mortality observations were made during the initial 4 hours of the tests and once daily thereafter at 24, 48, 72 and 96 hours. Test solution temperatures were kept within a range of 15°C ± 1.5°C and dissolved oxygen levels were maintained above 7.0 mg/L for the duration of the tests.

Acute lethality results for all tests were presented as 96-hour LC50s (concentrations of the samples lethal to 50% of the fish (ie. the average fish) after a 96-hour exposure), along with their 95% (or greater) confidence limits. Statistical comparisons between LC50s were undertaken using the Litchfield and Wilcoxon methods as outlined by Sprague and Fogels (1976). In all pulp mill effluent samples, LT50s (time to lethality for 50% of the test fish) were calculated in the full strength mill effluent.

The methods and procedures used for these tests met all of the test requirements as outlined in the OME fish bioassay protocol (Craig et al., 1983).

# RESULTS

## 1. Acute Lethality

### (a) Field Exposure

Fish lethality was observed at a limited number of study sites during the 96 h exposure. Within 96 h, 16% of the brown trout had died at one of the study site controls (Pither's Point), whereas the other two sites were non-lethal. Brown trout mortality was also observed downstream of the International Falls STP discharge and offshore of the golf course on the American side of the river, with 12 and 20% of the fish found dead at each of these sites, respectively (Table 1).

Fathead minnow mortality of 8% was observed at the plume upwelling of the Fort Frances mill diffuser during a 48 h exposure (Table 2). No other fathead minnow mortality was observed.

### (b) Laboratory Bioassays

A comparison of brown trout and rainbow trout sensitivity to abietic acid and the Boise Cascade mill effluents is presented in Appendices B & C. During the in situ exposure, the LC50 of the 4 composite samples of the Fort Frances mill effluent ranged from 29-43% over the 5-day study (Table 3). None of those samples met the Ontario Government toxicity test requirement for pulp and paper mill wastes of at least 50% fish survival in a 100% effluent concentration. The time for 50% of the fish to die in a full strength sample of that waste was calculated to be 8-10 hours.

There was no fish mortality observed in bioassays of the Boise Cascade International Falls mill effluent during the August study (Table 4).

TABLE 1: The % Mortality for Brown Trout Fingerlings Exposed on the Canadian and American sides of the Rainy River Downstream of the Boise Cascade Mills During the Period from August 24-28, 1986 (Study Days 1-5, respectively).

A) Control Fish

| Site # | Description | Mortality (%) |
|---|---|---|
| C-1 | Control - Island NW of Gash Point in Rainy Lake | 0 |
| C-2 | Control - Pithers Point | 16 |
| C-3 | Control - Log Boom 300m Upstream of International Bridge | 0 |

B) Exposure Fish

| | CANADIAN SIDE | | | AMERICAN SIDE | | |
|---|---|---|---|---|---|---|
| Distance Downstream from Power Dam (m) | Site # | Description | Mortality (%) | Site # | Description | Mortality (%) |
| 200 | | | | A | 15m downstream of Mill Diffuser[1] | 0 |
| 250 | 5 | Hydro Tower Peninsula | 0 | B | 65m downstream of Mill Diffuser[1] | 0 |
| 1100 | 6 | Adjacent 1st Set of Islands Downstream of Mill[2] | 0 | C | Adjacent 1st Set of Islands downstream of Mill[1] | 0 |
| 1950 | 7 | Fort Frances STP-30m downstream of Diffuser | 0 | | | |

Continued..........

[1] Mill refers to Boise Cascade International Falls Mill.

[2] Mill refers to Boise Cascade Fort Frances Mill.

TABLE 1 - Cont'd...

| B) Exposure Fish | CANADIAN SIDE | | | AMERICAN SIDE | | |
|---|---|---|---|---|---|---|
| Distance Downstream from Power Dam (m) | Site # | Description | Mortality (%) | Site # | Description | Mortality (%) |
| 3000 | | | | D | International Falls STP-30m Downstream of Diffuser | 12 |
| 4250 | 8 | Downstream of Canadian Greenhouses | 0 | E | Shore opposite Canadian Greenhouses | 0 |
| 4850 | 9 | 1st Major Bend Downstream | 0 | F | 1st Major Bend Downstream | cage missing[3] |
| 7200 | 10 | Shore opposite American Golf Course | 0 | G | Adjacent to Golf Course | 20 |

[3] Cage missing on day fish arrived, therefore remaining brown trout used for separate exposure at Big Fork River.

TABLE 2: The % Mortality for Fathead Minnows Exposed on the Canadian and American sides of the Rainy River Downstream of the Boise Cascade Mills During the Period from August 24-28, 1986 (Study Days 1-5, respectively)

A) Control Fish

| Site # | Description | Mortality (%) |
|---|---|---|
| C-1 | Control - Island NW of Gash Point in Rainy Lake | 0 |
| C-4 | Immediately downstream of Power Dam Spillway (48 h exposure - Day 3-5)[1] | 0 |

B) Exposure Fish

| | CANADIAN SIDE | | | AMERICAN SIDE | | |
|---|---|---|---|---|---|---|
| Distance Downstream from Power Dam (m) | Site # | Description | Mortality (%) | Site # | Description | Mortality (%) |
| 50 | 4 | Mill Diffuser Plume Upwelling (48 h - Day 3-5)[2] | 8 | | | |
| 4850 | 9 | 1st Major Bend Downstream | 0 | F | 1st Major Bend Downstream (72 h exposure - Day 2-5)[3] | 0 |

[1] Control involving fish maintained in same manner as those exposed at Site 4 on study day 3.

[2] Plume not visible on day cage positions set (Sat. Aug. 23/86) - and not located until afternoon of Study Day 2 - exposure commenced at 900 h on Day 3.

[3] Cage missing on day fish arrived (Study Day 1) - exposure in new cage commenced on the following day (Study Day 2).

TABLE 3: Laboratory Bioassay Results for the Boise Cascade (Fort Frances) Diffuser Effluent from August 24-28, 1986 (Study Days 1-5, respectively) using Rainbow Trout Test Fish.

| Sample Type | Sample Day | 96-h Bioassay LC50[1] (% V/V) | Fish-Mortality/Test-Solution | | |
|---|---|---|---|---|---|
| | | | Effluent Concentration (% V/V)[3] | Fish Mortality (%) | LT50(h)[2] for 100% Effluent |
| 24-h composite | 1-2 | 43 | 100 | 100 | 8 |
| | | (38, 48)[4] | 65 | 100 | |
| | | | 32 | 10 | |
| | | | 18 | 0 | |
| 24-h composite | 2-3 | 31 | 100 | 100 | 10 |
| | | (25,38) | 65 | 100 | |
| | | | 32 | 60 | |
| | | | 18 | 0 | |
| 24-h composite | 3-4 | 29 | 100 | 100 | 10 |
| | | (24, 35) | 65 | 100 | |
| | | | 32 | 70 | |
| | | | 18 | 0 | |
| 20-h composite | 4-5 | 35 | 100 | 100 | 10 |
| | | (29, 43) | 65 | 100 | |
| | | | 32 | 40 | |
| | | | 18 | 0 | |

Mean LC50 = 34.5 range = 29-43
S.D. = ± 6.2 N = 4

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[1] LC50 results calculated using the Spearman-Karber or Binomial Test Method.
[2] LT50 - time required to produce 50% fish lethality in the 100% effluent.
[3] % V/V represents: volume of effluent/total volume including diluant, expressed as a percentage.
[4] Upper and lower 95% confidence levels, respectively.

TABLE 4: Laboratory Bioassay Results for the Boise Cascade (International Falls) Diffuser Effluent from August 24-28, 1986 (Study Days 1-5, respectively), using Rainbow Trout Test Fish.

| Sample Type | Sample Day | 96 h Bioassay LC50[1] (% V/V) | Fish-Mortality/Test-Solution | | |
|---|---|---|---|---|---|
| | | | Effluent Concentration (% V/V)[3] | Fish Mortality (%) | LT50(h)[2] for 100% Effluent |
| Grab | 2 | >100 | 100 | 0 | >96 |
| | | | 65 | 0 | |
| | | | 32 | 0 | |
| Grab | 3 | >100 | 100 | 0 | >96 |
| | | | 65 | 0 | |
| | | | 32 | 0 | |
| 24-h composite | 3-4 | >100 | 100 | 0 | >96 |
| | | | 65 | 0 | |
| | | | 32 | 0 | |
| Grab | 5 | >100 | 100 | 0 | >96 |
| | | | 65 | 0 | |
| | | | 32 | 0 | |

[1] Results calculated using the Spearman-Karber or Binomial Test Method.

[2] LT50 - time required to produce 50% fish lethality in the 100% effluent.

[3] % V/V represents: volume of effluent/total volume including diluant, expressed as a percentage.

[4] Grab samples collected at 1230 h and composite was collected from noon to noon on the sample days cited in the above table.

### (c) Effluent Contaminants and Rainy River Water Quality

#### i) Total Reactive Phenolics

The International Falls mill effluent had phenolic levels which were consistently lower (4.2-8.0 µg/L) in comparison with 3 of 4 levels in the Fort Frances mill effluent (130-225 µg/L). The exception occurred in the day 1-2 composite sample, with phenolics in the Fort Frances mill effluent measured at 3.0 µg/L (Appendix D).

The levels of total reactive phenolics in the river downstream of both mills were not significantly greater than background levels upstream of the power dam, with the exception of 3-12 fold greater levels (7.6-32 µg/L) for samples collected in the Fort Frances diffuser upwelling (Site 4).

#### ii) Resin Acids

Total resin acid levels in the Fort Frances mill effluent were lower than measured previously in this waste, with levels ranging from 630-2070 µg/L over the 5-day study. Historically, abietic acid has been the principal resin acid in the effluent, with for example, 2270 µg/L in a January 29, 1986 sample (Table 5). However, in this study, the levopimaric species was present in concentrations equivalent to between 30-100% of total resin acid values (Table 5).

The total resin acid level in a reference test sample collected January 29, 1986 was 3635 µg/L. Higher resin acid levels in the winter are not unusual because lower treatment efficiencies cause a slower rate of contaminant degradation in a secondary lagoon than observed during summertime operations.

Resin acid levels in the Boise Cascade International Falls effluent ranged from non-detectable to 400 µg/L, which is low in comparison to the Fort Frances mill effluent (Table 5).

**TABLE 5:** **Resin Acid Concentrations in the Boise Cascade (Fort Frances and International Falls) Diffuser Effluents and Loadings to the Rainy River, August 24-28, 1986 (Study Days 1-5, respectively).**

| | Resin Acid Concentrations (µg/L) in the Boise Cascade (Fort Frances) Effluent on Study Days | | | | | Resin Acid Concentrations (µg/L) in the Boise Cascade (International Falls) Effluent on Study Days | | | |
|---|---|---|---|---|---|---|---|---|---|
| Resin Acid Species | 1-2 | 2-3 | 3-4 | 4-5 | Ref. | 1-2 | 3 | 3-4 | 5 |
| Pimaric | 67 | 70 | nd | 23 | 150 | nd | 10 | nd | nd |
| Sandaracopimaric | 56 | 60 | nd | 18 | nd | nd | nd | nd | nd |
| Levopimaric | 695 | 700 | 729 | 322 | 70 | nd | nd | nd | nd |
| Isopimaric | 106 | 110 | nd | 33 | 445 | nd | nd | 13 | nd |
| Neoabietic | 130 | 120 | nd | 44 | 40 | nd | nd | nd | nd |
| Abietic | 472 | 560 | nd | 120 | 2270 | nd | nd | 168 | nd |
| Dehydroabietic | nd | 450 | nd | 70 | 660 | nd | nd | 219 | nd |
| Totals | 1526 | 2070 | 729 | 630 | 3635 | nd | 10 | 400 | - |
| Total Loadings (kg/day) | 116.7 | 159.6 | 56.2 | 47.9 | - | - | 1.3 | 50.5 | - |

NOTE:
(1) The detection level for all resin acids: 10 µg/L.
(2) nd - not detected.
(3) Palustric and Levopimaric Acids are reported as one result.
(4) Ref. - reference levels were measured in a sample collected Jan. 29/86.
(5) For the Boise Cascade (Fort Frances) effluent, all samples were 24 h composites taken from noon until noon on the study days indicated in the above table.
(6) For the Boise Cascade (International Falls) effluent, Day 1-2 sample collected from 2100 h August 24 to 1300 h August 25/86 (16 h composite). Day 3 + 5 samples were grabs collected at 1230 h August 26/86 and August 28/86, respectively. Day 3-4 sample was a 24 h composite collected from noon to noon.
(7) Loadings based on daily discharge volumes for the Fort Frances mill in Appendix K and International Falls in Appendix L.

Resin acids detected in the Rainy River were limited to monochloroabietic and levopimaric acids on only a few occasions (Appendix E). No values exceeded 80 µg/L.

### iii) Organosulfides

There were large fluctuations in total organosulfide concentrations in both Boise Cascade effluents. Concentrations in the Canadian mill effluent varied from 15-436 µg of total sulfides/L (Table 6), while near non-detectable levels were present in three samples and 282 µg/L in the 4th sample from the American mill (Table 7). In nearly all cases in which sulfide levels were greater than 20 ug/L, 90% or more of the sulfides were present as hydrogen sulfide. All of the samples were unfiltered and no attempt was made to determine the fraction of the sulfides which were associated with particulate matter in the effluents.

Sulfides were not detected in any of the samples downstream of either mill during the first 3 days of the study.

### iv) Chlorophenols (CP's)

The highest concentrations of chlorophenols in both mill effluents were in the 2,4,6-trichlorophenol (2,4,6-TCP) form (Table 8). Effluent concentrations ranged from 150-700 ng/L and 2900-16,000 ng/L for 2,4,6-TCP in the Boise Cascade International Falls and Fort Frances operations, respectively. The higher levels in the Canadian mill are consistent with those found in other full bleached Kraft mill operations. Traces of pentachlorophenol (PCP) were detected in 2 of 4 samples from the American mill, while levels of 330-980 ng/L were measured in the Canadian operation. The only other species of chlorophenols found in an effluent sample were the 2,4,5 TCP and 2,3,5,6-Tetra CP forms, both measured in 1 of 4 samples from the Canadian operation.

TABLE 6: Organosulfur Compound Concentrations in the Boise Cascade (Fort Frances) Diffuser Effluent August 24-28, 1986 (Study Days 1-5, respectively).

| | Organosulfur Concentrations (ug/L) on Study Days | | | |
|---|---|---|---|---|
| Organosulfur Species | 1-2 | 2-3 | 3-4 | 4-5 |
| Carbonyl Sulfide (see note 4 below) | 10.8 | 9.4 | 1.5 | 4.4 |
| Carbon Disulfide | 2.1 | 1.9 | 0.7 | 0.5 |
| Dimethyl Disulfide | 1.4 | 0.4 | 1.1 | 0.5 |
| Dimethyl Sulfide | 1.5 | 2.2 | 0.3 | 0.6 |
| Ethyl Mercaptan | nd | nd | nd | nd |
| Hydrogen Sulfide | 270.0 | 422.0 | 39.0 | 9.3 |
| Methyl Mercaptan | nd | nd | nd | nd |
| Sulfur Dioxide (see note 4 below) | - | - | - | - |
| Thiophene | nd | nd | nd | nd |
| Totals | 285.8 | 435.9 | 42.6 | 15.3 |

NOTE: (1) Test results are considered as minimum values.

(2) Detection level for all sulfides: 0.30 µg/L.

(3) nd - not detected.

(4) The test method does not differentiate between carbonyl sulfide and sulfur dioxide. (- indicates included with carbonyl sulfide.)

(5) All samples are 24-h composites taken from noon until noon on the study days indicated in the above table.

TABLE 7: Organosulfur Compound Concentrations in the Boise Cascade (International Falls) Diffuser Effluent August 24-28, 1986 (Study Days 1-5, respectively).

| Organosulfur Species | Organosulfur Concentrations (ug/L) on Study Days | | | |
|---|---|---|---|---|
| | 1-2 | 3 | 3-4 | 5 |
| Carbonyl Sulfide (see note 4 below) | nd | nd | 2.2 | 0.3 |
| Carbon Disulfide | nd | nd | nd | 0.3 |
| Dimethyl Disulfide | nd | 0.4 | nd | 0.3 |
| Dimethyl Sulfide | nd | nd | nd | nd |
| Ethyl Mercaptan | nd | nd | nd | nd |
| Hydrogen Sulfide | nd | nd | 280.0 | nd |
| Methyl Mercaptan | nd | nd | nd | nd |
| Sulfur Dioxide (see note 4 below) | nd | nd | - | - |
| Thiophene | nd | nd | nd | nd |
| Totals | nd | 0.4 | 282.2 | 0.9 |

NOTE: (1) Test results are considered as minimum values.
(2) Detection level for all sulfides: 0.30 μg/L.
(3) nd - not detected.
(4) The test method does not differentiate between carbonyl sulfide and sulfur dioxide. (- indicates included with carbonyl sulfide.)
(5) Day 1-2 sample collected from 2100-h August 24 to 1300-h August 25/86 (16-h composite). Day 3 + 5 samples were grabs collected at 1230-h August 26/86 and August 28/86, respectively. Day 3-4 sample was a 24-h composite collected from noon to noon.

TABLE 8: Chlorophenol Concentrations in the Boise Cascade (Fort Frances & International Falls) Diffuser Effluents, August 24-28, 1986 (Study Days 1-5, respectively).

| Chlorophenol Species | Chlorophenol Concentrations (ng/L) in the Boise Cascade (Fort Frances) Effluent on Study Days | | | | Chlorophenol Concentrations (ng/L) in the Boise Cascade (International Falls) Effluent on Study Days | | | |
|---|---|---|---|---|---|---|---|---|
| | 1-2 | 2-3 | 3-4 | 4-5 | 1-2 | 3 | 4 | 5 |
| 2,4,6 - Trichlorophenol | 16000 | 11900 | 5300 | 2900 | 700 | 450 | 150 | 240 |
| 2,4,5 - Trichlorophenol | 230 | nd | nd | nd | nd | nd | nd | nd |
| 2,3,5,6 - Tetrachlorophenol | nd | nd | 700 | nd | nd | nd | nd | nd |
| Pentachlorophenol | 980 | 860 | 360 | 330 | 50 | 50 | nd | nd |

| Chlorophenol Analyses Undertaken | | Detection Levels (ng/L) |
|---|---|---|
| 2,3,4 - Trichlorophenol | (2,3,4 TCP) | 100 |
| 2,4,5 - Trichlorophenol | (2,4,5 TCP) | 50 |
| 2,4,6 - Trichlorophenol | (2,4,6 TCP) | 50 |
| 2,3,4,5 - Tetrachlorophenol | (2,3,4,5 TTCP) | 50 |
| 2,3,5,6 - Tetrachlorophenol | (2,3,5,6 TTCP) | 50 |
| 2,3,4,6 - Tetrachlorophenol | (2,3,4,6 TTCP) | 50 |
| Pentachlorophenol | (Penta CP) | 50 |

NOTE: (1) All samples were 24 h composites taken from noon until noon on the study days indicated in the above table, except as noted in (2).

(2) For the Boise Cascade (International Falls) effluent, Day 1-2 sample collected from 2100 h August 24 to 1300 h August 25/86 16-h composite). Day 3 + 5 samples were grabs collected at 1230 h August 26/86 and August 28/86, respectively. Day 3-4 sample was a 24 h composite collected from noon to noon.

(3) nd - not detected.

(4) The retention time for the analyses of 2,3,4,5 - and and 2,3,4,6 - tetrachlorophenol is the same; hence 2,3,4,5 - TTCP results would have also included 2,3,4,6 TTCP levels.

Pentachlorophenol levels in the International Falls sewage treatment plant (STP) effluent were 3-5 fold greater than the highest value measured in the International Falls pulp mill, while PCP in the Canadian STP and pulp mill effluent fell within a similar concentration range (Tables 8 & 9). On the other hand, for 2,4,6-TCP, the International Falls STP did not contain detectable levels, while concentrations in the Fort Frances STP effluent were as high as 1100 ng/L (Tables 8 & 10). In regard to chlorophenol loadings, levels discharged by the pulp mills were 20-100 times greater than quantities put out by their corresponding town STPs (Tables (9 & 10).

Pentachlorophenol was not commonly found beyond exposure site 7 on the Canadian side of the river (Table 11). Levels on the American side could be measured as far downstream as the golf course (site G). In one case (on study day 5), the presence of PCP appeared to be a direct result of the International Falls STP discharge, for it was not detected in the American mill effluent (Table 8) or on the American side of the river upstream of the STP (Table 12). Concentrations of 2,4,6-TCP were measured throughout the study area on both sides of the river. Levels on the American side would appear to be solely due to the International Falls mill effluent while Canadian sources downstream of the Fort Frances STP are likely due to the pulp mill and STP effluents. The highest river concentrations of 2,4,6-TCP occurred in the diffuser upwelling of the Fort Frances mill, with levels of 340-690 ng/L (Table 11). Upon reaching the first set of islands downstream of the mill diffusers, levels of 2,4,6-TCP had decreased appreciably due to vertical mixing of the effluent in the river water column and remained consistent throughout the rest of the study area.

### v) Phenoxy Acids

The phenoxy acid most commonly found in the pulp mill effluents was 2,4-Dichlorophenoxybutyric Acid (2,4-DB), with levels present in half of the Canadian and all of the American mill

TABLE 9: Chlorophenol Concentrations and Loadings for the Fort Frances and International Falls STP Final Effluents, August 26-28, 1986 (Study Days 3-5, respectively).

| | Chlorophenol Concentrations (ng/L) in the Fort Frances STP on Study Days | | | Chlorophenol Concentrations (ng/L) in the International Falls STP on Study Days | | |
|---|---|---|---|---|---|---|
| Chlorophenol Species | 3 | 4 | 5 | 3 | 4 | 5 |
| 2,4,6 - Trichlorophenol | 740 | 920 | 1100 | nd | nd | nd |
| Pentachlorophenol | 760 | 640 | 600 | 260 | 170 | 260 |
| | Chlorophenol Loadings (g/d) from the Fort Frances STP on Study Days | | | Chlorophenol Loadings (g/d) from the International Falls STP on Study Days | | |
| Chlorophenol Species | 3 | 4 | 5 | 3 | 4 | 5 |
| 2,4,6 - Trichlorophenol | 4.9 | 6.1 | 7.3 | – | – | – |
| Pentachlorophenol | 5.0 | 4.2 | 4.0 | 1.4 | 0.9 | 1.4 |

| Chlorophenol Analyses Undertaken | | Detection Levels (ng/L) |
|---|---|---|
| 2,3,4 - Trichlorophenol | (2,3,4 TCP) | 100 |
| 2,4,5 - Trichlorophenol | (2,4,5 TCP) | 50 |
| 2,4,6 - Trichlorophenol | (2,4,6 TCP) | 50 |
| 2,3,4,5 - Tetrachlorophenol | (2,3,4,5 TTCP) | 50 |
| 2,3,5,6 - Tetrachlorophenol | (2,3,5,6 TTCP) | 50 |
| 2,3,4,6 - Tetrachlorophenol | (2,3,4,6 TTCP) | 50 |
| Pentachlorophenol | (Penta CP) | 50 |

NOTE: (1) All collections were grab samples.
(2) nd - not detected.
(3) Loadings from the Fort Frances and International Falls STP's are based on the average daily flows for August 1986 of 6.6 x $10^3 m^3$/day and 5.2 x $10^3 m^3$/day, respectively.

TABLE 10: Chlorophenol Loadings to the Rainy River from the Boise Cascade (Fort Frances & International Falls) Effluents During August 24–28, 1986 (Study Days 1–5, respectively).

| | Chlorophenol Loadings (g/d) from the Boise Cascade (Fort Frances) Effluent on Study Days | | | | Chlorophenol Loadings (g/d) from the Boise Cascade (International Falls) Effluent on Study Days | | | |
|---|---|---|---|---|---|---|---|---|
| Chlorophenol Species | 1–2 | 2–3 | 3–4 | 4–5 | 1–2 | 3 | 3–4 | 5 |
| 2,4,6 – Trichlorophenol | 1224 | 925 | 4120 | 220 | 95 | 58 | 19 | 31 |
| 2,4,5 – Trichlorophenol | 18 | – | – | – | – | – | – | – |
| 2,3,5,6 – Tetrachlorophenol | – | – | 54 | – | – | – | – | – |
| Pentachlorophenol | 75 | 67 | 28 | 25 | 6.8 | 6.5 | <6.3 | <6.5 |
| Total Loadings (g/d) | 1317 | 992 | 494 | 245 | 101.8 | 64.5 | 19 | 31 |

NOTE: (1) These loadings were calculated using chlorophenol concentrations from Table 8 and effluent flows from Appendices K & L.

(2) Total Loadings are considered to be minimum values only.

TABLE 11: Chlorophenol Concentrations on the Canadian Side of the Rainy River Up and Downstream of the Boise Cascade (Fort Frances) Mill Diffuser from August 24-28, 1986 (Study Days 1-5, respectively).

| Study Day/ Chlorophenol Species | Concentrations (ng/L) at Study Sites | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C-1 | C-2 | C-3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Day 1 | | | | | | | | | | |
| 2,4,6 - TCP | nd | nd | nd | – | 150 | 150 | 160 | nd | nd | 110 |
| Day 2 | | | | | | | | | | |
| 2,4,6 - TCP | nd | nd | nd | – | nd | 180 | nd | nd | nd | nd |
| Penta CP | nd | nd | nd | – | 60 | 80 | 90 | nd | nd | 80 |
| Day 3 | | | | | | | | | | |
| 2,4,6 - TCP | – | nd | nd | 420 | 220 | 200 | 170 | 170 | 170 | 180 |
| Penta CP | – | nd | 50 | 70 | 90 | 100 | nd | 80 | nd | nd |
| Day 4 | | | | | | | | | | |
| 2,4,6 - TCP | – | nd | nd | 340 | 160 | 100 | 130 | 130 | 140 | 100 |
| Day 5 | | | | | | | | | | |
| 2,4,6 - TCP | nd | nd | nd | 690 | 170 | 170 | 150 | 130 | 120 | 100 |
| Penta CP | nd | nd | nd | 60 | nd | nd | nd | nd | nd | nd |

| Chlorophenol Analyses Undertaken | | Detection Levels (ng/L) |
|---|---|---|
| 2,3,4 - Trichlorophenol | (2,3,4 TCP) | 100 |
| 2,4,5 - Trichlorophenol | (2,4,5 TCP) | 50 |
| 2,4,6 - Trichlorophenol | (2,4,6 TCP) | 50 |
| 2,3,4,5 - Tetrachlorophenol | (2,3,4,5 TTCP) | 50 |
| 2,3,5,6 - Tetrachlorophenol | (2,3,5,6 TTCP) | 50 |
| 2,3,4,6 - Tetrachlorophenol | (2,3,4,6 TTCP) | 50 |
| Pentachlorophenol | (Penta CP) | 50 |

nd - not detected

– - sample not collected due to rough waters at C-1 and no cage installed at site 4 until day 3.

NOTE: The retention time in the analyses of 2,3,4,5- and 2,3,4,6-tetrachlorophenol is the same; hence 2,3,4,5 TTCP results would also include 2,3,4,6 TTCP levels.

TABLE 12: **Chlorophenol Concentrations on the American Side of the Rainy River Up and Downstream of the Boise Cascade (International Falls) Mill Diffuser from August 24-28, 1986 (Study Days 1-5, respectively).**

| Study Day/ Chlorophenol Species | Concentrations (ng/L) at Study Sites | | | | | | |
|---|---|---|---|---|---|---|---|
| | A | B | C | D | E | F | G |
| Day 1 | | | | | | | |
| 2,4,6 - TCP | 100 | 120 | 90 | 70 | 100 | 100 | 70 |
| Day 2 | | | | | | | |
| 2,4,6 - TCP | nd | 110 | 105 | 100 | 95 | nd | nd |
| Penta CP | 80 | nd | nd | nd | nd | nd | nd |
| Day 3 | | | | | | | |
| 2,4,6 - TCP | 150 | 100 | 120 | 100 | nd | 140 | 140 |
| Penta CP | 80 | nd | nd | nd | nd | nd | 50 |
| Day 4 | | | | | | | |
| 2,4,6 - TCP | 120 | 120 | 100 | 100 | 90 | 90 | 100 |
| Penta CP | 90 | nd | 70 | nd | 70 | nd | 50 |
| Day 5 | | | | | | | |
| 2,4,6 - TCP | 290 | 220 | 100 | 80 | 90 | 80 | 90 |
| Penta CP | nd | nd | nd | nd | 60 | 50 | 60 |

| Chlorophenol Analyses Undertaken | | Detection Levels (ng/L) |
|---|---|---|
| 2,3,4 - Trichlorophenol | (2,3,4 TCP) | 100 |
| 2,4,5 - Trichlorophenol | (2,4,5 TCP) | 50 |
| 2,4,6 - Trichlorophenol | (2,4,6 TCP) | 50 |
| 2,3,4,5 - Tetrachlorophenol | (2,3,4,5 TTCP) | 50 |
| 2,3,5,6 - Tetrachlorophenol | (2,3,5,6 TTCP) | 50 |
| 2,3,4,6 - Tetrachlorophenol | (2,3,4,6 TTCP) | 50 |
| Pentachlorophenol | (Penta CP) | 50 |

nd - not detected

NOTE: The retention time in the analyses of 2,3,4,5- and 2,3,4,6-tetrachlorophenol is the same; hence 2,3,4,5 TTCP results would also include 2,3,4,6 TTCP levels.

samples (Table 13). The 2,4-Dichlorophenoxypropionic Acid (2,4-DP) was also present in 2 or more samples from each mill. Daily phenoxy acid loadings from the mills are presented in Table 14.

The common herbicides 2,4-D and 2,4,5-T were detected in each of the mill effluents. The 2,4,5-T species was present in the day 3-4 composite samples from both mills, and since it is now banned for use in Canada, a second sample of the effluent collected on day 3 was tested. However, the presence of 2,4,5-T could not be confirmed in that sample.

No phenoxy acids were detected in the river during sampling runs of all fish exposure sites on study days 3 or 4.

### vi) Dioxins and Furans

The detection level for dioxins and furans previously indicated by the lab as attainable (80 pg/L), was achieved for 1 of 8 samples collected over 4 days, and only for the tetrachlorodibenzodioxin (TCDD) and tetrachlorodibenzofuran (TCDF) congeners in that case. In the composite sample (August 24-25th), for which low detection levels were achieved, TCDD was not detected above 80 pg/L and TCDF was found at 80 pg/L (ppq) in the Boise Cascade Fort Frances final effluent. In the August 24-25th samples, none of the other dioxin or furan species were found in either mill effluent above detection levels, which ranged from 100-2100 pg/L (Table 15).

The only other samples in which dioxins and furans were found, occurred in the August 27-28th collection and in those cases only the heptachlorinated and octachlorinated dioxins and furans were detected (Table 16).

Dioxins and furans were not detected in a composite sample of the Fort Frances mill effluent collected August 25-26th and in an August 26th grab sample from the International Falls mill.

TABLE 13: Phenoxy Acid Concentrations in the Boise Cascade (Fort Frances and International Falls) Diffuser Effluents, August 24-28, 1986 (Study Days 1-5, respectively).

| | Phenoxy Acid Concentrations (ng/L) in the Boise Cascade (Fort Frances) Effluent on Study Days | | | | Phenoxy Acid Concentrations (ng/L) in the Boise Cascade (International Falls) Effluent on Study Days | | | |
|---|---|---|---|---|---|---|---|---|
| Phenoxy Acid Species | 1-2 | 2-3 | 3-4 | 4-5 | 1-2 | 2-3 | 3-4 | 4-5 |
| Dicamba | nd | 100 | nd | nd | nd | nd | nd | nd |
| 2,4 - DP | nd | 970 | nd | 240 | 430 | nd | 140 | 490 |
| 2,4 - D | nd | 310 | nd | nd | nd | nd | 330 | nd |
| 2,4,5 - T | nd | nd | 320 | nd | nd | nd | 80 | nd |
| Silvex | nd | nd | nd | nd | nd | nd | nd | 210 |
| 2,4 - DB | nd | nd | 5700 | 1270 | 2000 | 3000 | 1640 | 3600 |
| Picloram | nd | 600 | nd | nd | nd | 600 | nd | nd |

| Phenoxy Acid Analyses Undertaken | Detection Levels (ng/L) |
|---|---|
| Dicamba | 100 |
| 2,4 - Dichlorophenoxypropionic Acid (2,4-DP) | 100 |
| 2,4 - Dichlorophenoxyacetic Acid (2,4-D) | 100 |
| Silvex | 50 |
| 2,4,5 - Trichlorophenoxyacetic Acid (2,4,5-T) | 50 |
| 2,4 - Dichlorophenoxybutyric Acid (2,4-DB) | 200 |
| Picloram | 100 |

NOTE: For the Boise Cascade (International Falls) effluent, Day 1-2 sample collected from 2100 h August 24 to 1300 h August 25/86 (16 h composite). Day 3 + 5 samples were grabs collected at 1230 h August 26/86 and August 28/86, respectively. Day 3-4 sample was a 24 h composite collected from noon to noon.

nd - not detected.

TABLE 14: **Phenoxy Acid Loadings to the Rainy River from the Boise Cascade (Fort Francis & International Falls) Diffuser Effluents, August 24-28, 1986 (Study Days 1-5, respectively).**

| Phenoxy Acid Species | Phenoxy Acid Loadings (g/d) from the Boise Cascade (Fort Frances) Effluent on Study Days | | | | Phenoxy Acid Loadings (g/d) from the Boise Cascade (International Falls) Effluent on Study Days | | | |
|---|---|---|---|---|---|---|---|---|
| | 1-2 | 2-3 | 3-4 | 4-5 | 1-2 | 3 | 3-4 | 5 |
| Decamba | – | 7.7 | – | – | – | – | – | – |
| 2,4 - DP | – | 75 | – | 18 | 58 | – | 18 | 63 |
| 2,4 - D | – | 24 | – | – | – | – | 42 | – |
| 2,4,5 - T* | – | – | 25* | – | – | – | 10* | – |
| Silvex | – | – | – | – | – | – | – | 27 |
| 2,4 - DB | – | – | 440 | 96 | 270 | 389 | 207 | 464 |
| Picloram | – | 46 | – | – | 31 | 20 | – | 101 |
| Total Loadings (g/d) | – | 153 | 465 | 114 | 359 | 409 | 277 | 655 |

NOTE: (1) These loadings were calculated using phenoxy acid concentrations from Table 13 and effluent discharge volumes from Appendices K & L.

(2) Total Loadings are considered to be minimum values only.

* denotes presence not confirmed in follow-up mass specrometric analysis of a second sample.

TABLE 15: Concentrations of Chlorinated Dibenzo-p-dioxins (CDD) and Chlorinated Dibenzofurans (CDF)* in the Effluents of the Boise Cascade Mills on August 24-25, 1986.

| Sample Description: | Boise Cascade<br>Fort Frances<br>Final Effluent | Boise Cascade<br>International Falls<br>Final Effluent |
|---|---|---|
| Collection Time: | 24-h composite<br>noon August 24<br>to noon August 25 | 15-h composite<br>2100-h August 24<br>to noon August 25 |
| CDD | | |
| 4CDD | ND (0.08) | ND (0.20) |
| 5CDD | ND (0.24) | ND (2.1) |
| 6CDD | ND (0.69) | ND (0.35) |
| 7CDD | ND (0.21) | ND (0.30) |
| 8CDD | ND (0.45) | ND (0.16) |
| CDF | | |
| 4CDF | $0.08^1$ | ND (0.23) |
| 5CDF | ND (0.16) | ND (0.18) |
| 6CDF | ND (0.18) | ND (0.10) |
| 7CDF | ND (0.64) | ND (0.28) |
| 8CDF | ND (0.18) | ND (0.25) |
| Internal Standard Recoveries (%) | | |
| $^{13}C_{12}$-2,3,7,8-TCDD | 56 | 62 |
| $^{13}C_{12}$-8CDD | 73 | 63 |

* All data in parts-per-trillion (ppt;ng/L), corrected for recovery of internal standards. 'ND' indicates not detected. Single isomer detection limits are given in brackets. Superscripts indicate number of isomers observed.

TABLE 16: **Concentrations of Chlorinated Dibenzo-p-dioxins (CDD) and Chlorinated Dibenzofurans (CDF)* in the Effluents of the Boise Cascade Mills on August 27-28, 1986.**

| Sample Description: | Boise Cascade<br>Fort Frances<br>Final Effluent | Boise Cascade<br>International Falls<br>Final Effluent |
|---|---|---|
| Collection Time: | 24 h composite<br>noon August 27<br>to noon August 28 | grab samples<br>at 1230<br>August 28 |
| CDD | | |
| 4CDD | ND (0.70) | ND (0.31) |
| 5CDD | ND (1.2) | ND (4.8) |
| 6CDD | ND (1.1) | ND (0.62) |
| 7CDD | $0.63^2$ | ND (0.20) |
| 8CDD | $0.79^1$ | $0.29^1$ |
| CDF | | |
| 4CDF | ND (0.46) | ND (0.30) |
| 5CDF | ND (0.81) | ND (0.37) |
| 6CDF | ND (0.47) | ND (0.15) |
| 7CDF | $0.14^1$ | ND (0.22) |
| 8CDF | $0.50^1$ | ND (0.12) |
| Internal Standard Recoveries (%) | | |
| $^{13}C_{12}$-2,3,7,8-TCDD | 21 | 27 |
| $^{13}C_{12}$-8CDD | 78 | 70 |

* All data in parts-per-trillion (ppt;ng/L), corrected for recovery of internal standards. 'ND' indicates not detected. Single isomer detection limits are given in brackets. Superscripts indicate number of isomers observed.

The detection levels for those analyses ranged from 90-830 pg/L. The lowest detection level for the tetra CDD and CDFs in those samples was 200 pg/L, while the internal standard recovery was 19% for 2,3,7,8-TCDD.

For the August 26-27th composite samples, the dioxin/furan detection levels in the mill effluents ranged from 110-3200 pg/L. A 110 pg/L detection level was obtained for tetra CDD species in the International Falls sample, along with a corresponding Internal Standard Recovery of 87% for 2,3,7,8 TCDD. No dioxins or furans were detected in the two effluent samples of August 26-27th.

### vii) Pesticides and Other Organochlorine Compounds

Low levels of pesticides were detected in both Boise Cascade effluents on each sampling day. The most consistently found compounds were endosulfan sulphate, DMDT Methoxychlor and pp-DDT and they were found in the International Falls mill effluent on 3 of 4 days. Two of those compounds, the endosulfan sulphate and DMDT Methoxychlor were measured at the highest levels of all (22) compounds for which analyses were undertaken (Appendix J). Endosulfan sulphate was also detected in 2 of 4 effluent samples from the Fort Frances mill (Appendix J).

Detectable levels of these compounds would not be expected in the Rainy River based on the values found in the effluents.

### viii) Dissolved Oxygen and Conductivity

Dissolved oxygen levels were not found below 7.6 mg/L at any of the cage sites during the study and therefore dissolved oxygen was not considered a problem in the 7.0 km stretch of river immediately downstream of the mills. Field data for the study are presented in Appendices F, G, H and I.

## 2. Chlorophenol Bioconcentration

Chlorophenol concentrations were detected in fish at only one site on the Canadian side of the river downstream of the Boise Cascade pulp mills (Table 17). Those levels occurred at a surface cage located directly over the effluent upwelling from the Fort Frances mill diffuser and included the highest bioconcentration levels of 2,4,6-trichlorophenol in fish analyzed in the study ($\bar{X}$±SD of 77.5 ng/g ±19.4). One of four samples from that site also contained the detection level value for pentachlorophenol (50 ng/g).

Chlorophenol residues were found in 5 of 34 samples of fish exposed downstream of the International Falls mill, and levels in each of those five samples were at or only slightly above detection levels. In only one case did more than one sample from a site have detectable chlorophenol levels. In that case, 2 of 5 samples from 30 m downstream of the International Falls STP, had 50 ng/g of pentachlorophenol. One of those samples also contained 50 ng/g of 2,4,6-trichlorophenol.

TABLE 17: Chlorophenol Residues in Composite Samples of Brown Trout and Fathead Minnows Caged on the Canadian and American Side of the Rainy River Downstream of the Boise Cascade Pulp Mills

I. Canadian side[1]

1. Fathead Minnow Data

| No. | Site Description | No. of Composite Samples | No. of Samples With Detectable Values | Composite Sample No. | Chlorophenol Residues (ng/g) 2,4,6-Tri-chlorophenol | Penta-chlorophenol | BCF* |
|---|---|---|---|---|---|---|---|
| 4 | Fort Frances Mill Diffuser Upwelling (48 h exposure) | 4 | 4 | 1 | 70 | nd | 145 (2,4,6-TCP) |
| | | | | 2 | 75 | nd | 155 (2,4,6-TCP) |
| | | | | 3 | 60 | nd | 124 (2,4,6-TCP) |
| | | | | 4 | 105 | 50 | 217 (2,4,6-TCP)<br>968 (penta CP) |

II. American side

1. Brown Trout Data

| No. | Site Description | No. of Composite Samples | No. of Samples With Detectable Values | Composite Sample No. | Chlorophenol Residues (ng/g) 2,4,6-Tri-chlorophenol | Penta-chlorophenol | BCF* |
|---|---|---|---|---|---|---|---|
| C | Adjacent 1st Set of Islands Downstream of International Falls Mill | 5 | 1 | 1 | 50 | nd | 468 (2,4,6-TCP) |
| D | International Falls STP - 30 m Downstream of Diffuser | 5 | 2 | 1 | nd | 50 | >1000 (penta CP) |
| | | | | 2 | 50 | 50 | 536 (2,4,6-TCP)<br>>1000 (penta CP) |
| G | Adjacent of American Golf Course | 5 | 1 | 1 | nd | 60 | 1125 (penta CP) |

Continued........

TABLE 17: (cont'd)

2. Fathead Minnow Data

| No. | Site Description | No. of Composite Samples | No. of Samples With Detectable Values | Composite Sample No. | Chlorophenol Residues (ng/g) 2,4,6-Trichlorophenol | Pentachlorophenol | BCF* |
|---|---|---|---|---|---|---|---|
| F | 1st Major Bend Downstream of the International Falls Mill | 4 | 1 | 1 | 50 | nd | 484 (2,4,6-TCP) |

Note: nd - not detected

Brown Trout exposed at all sites except site 2, while fathead minnow exposures limited to sites 4 and 9 on the Canadian side of the river and site F on the American Side.

*BCF - Bioconcentration Factor - the ratio of the measured residue of chlorophenol species in fish versus (ie. as compared to) the concentration of that substance in the water at the fish exposure site.

- Based on the average water concentration of the chlorophenol species over the last 3 exposure days, in which nd water concentrations were calculated as being ½ of the detection level.

# DISCUSSION

## 1. Acute Lethality

### (a) Field Exposure

There was no acute lethality observed at two of the three control sites. The lethality that did occur at the Pither's Point control site (16%) may have been due to the strong river currents at that site, even though attempts were made to place the cage in a relatively sheltered location. In particular, the strong river current combined with a starvation diet over the 96 h exposure likely overcame the stamina of the weaker fish in the cage, resulting in their demise. Likewise, the lethality observed downstream of the International Falls STP and the golf course may be due to a similar situation, even though a weedy sheltered area which appeared to be out of the strong river current, was selected at the golf course.

The 8% fish mortality in the Boise Cascade (Fort Frances) plume upwelling is not considered to be a significant response relative to control mortality (Table 2). A test response in the range of 50% mortality or more would be considered to be significant, for it would be a response from the average or stronger fish, rather than that of a few of the weaker individuals in the population. Based on the results of this study, the effluent plume from the American mill was not found to be acutely lethal, and in the case of the Fort Frances mill, essentially not acutely lethal.

The fathead minnow exposure in the Fort Frances mill upwelling lasted only 48 hours; nevertheless, it is considered as representative of a 96-h exposure, based on lab results. The 48-hour LC50s for the Fort Frances mill effluent were not significantly different ($p<0.05$) than the 96-h LC50s in 3 of 4 laboratory bioassays; and only slightly less toxic in the fourth case during this study (Table 18). Therefore, if the effluent quality remained consistent and significant mortality was expected

TABLE 18: A Comparison of LC50s at 48 & 96 h and Related Fish Mortality Data for Laboratory Bioassays of the Boise Cascade Fort Frances Mill Effluent from August 24-28, 1986 Study Days 1-5, respectively).

| Sample Day | Fish-Mortality/Test-Solution | | | 48 h Bioassay LC50[1] (% V/V)[2] | 96 h Bioassay LC50[1] (% V/V)[2] |
|---|---|---|---|---|---|
| | Effluent Concentration (% V/V)[2] | 48 h Fish Mortality (%) | 96 h Fish Mortality (%) | | |
| 1-2 | 100 | 100 | 100 | 46 | 43 |
| | 65 | 100 | 100 | (32, 65)[3] | (38, 48)[3] |
| | 32 | 0 | 10 | | |
| | 18 | 0 | 0 | | |
| 2-3 | 100 | 100 | 100 | 35 | 31 |
| | 65 | 100 | 100 | (29, 43) | (25, 38) |
| | 32 | 40 | 60 | | |
| | 18 | 0 | 0 | | |
| 3-4 | 100 | 100 | 100 | 40 | 29 |
| | 65 | 100 | 100 | (34, 47) | (24, 35) |
| | 32 | 20 | 70 | | |
| | 18 | 0 | 0 | | |
| 4-5 | 100 | 100 | 100 | 43 | 35 |
| | 65 | 100 | 100 | (38, 48) | (29, 43) |
| | 32 | 0 | 40 | | |
| | 18 | 0 | 0 | | |

[1] LC50 results calculated using the Spearman-Karber Method or Binomial Test Method.

[2] % V/V represents: volume of effluent/total volume including diluant, expressed as a percentage.

[3] Upper and lower 95% confidence levels, respectively.

to have occurred in the effluent upwelling, it would most likely have occurred within the first 48 hours of an exposure.

(b) Laboratory Bioassays

Based on the historical data of the Boise Cascade Fort Frances mill and chemical analyses during this study, two families of toxicants, sulfides and/or resin acids would appear to be potentially the most lethal components in the Fort Frances mill effluent.

i) Organosulfides

In this study, it was found that an effluent (from the Fort Frances mill) which was lethal, contained a 15 µg/L concentration of total sulfides; while a non-lethal (International Falls) effluent sample contained 272 µg/L.

The concentration of total sulfides in the Fort Frances mill effluent ranged from 15-436 µg/L, of which 75% or more was present as hydrogen sulfide. The LC50s of the two effluent samples with 15 and 436 µg/L concentrations of sulfides were 35 and 31%, respectively. Based on the fact that up to a 30-fold difference in sulfide levels produced no significant difference in effluent lethality, it would appear that in these two mill effluents, sulfides played at the most, a very minor role in acute lethality.

ii) Resin Acids (RA)

An LC50 of a complex effluent can be calculated by using the Toxic Unit (or Joint Toxicity) concept as outlined by Sprague (1970), if the lethality from each of its toxic components is additive. The most likely source of lethality in the Fort Frances mill waste is resin acids and there is considerable evidence that RA toxicity is additive (Taylor et al., 1988).

The theoretical RA contribution to effluent toxicity using the toxic unit (TU) concept involves their individual contributions as follows:

$$\text{TU} = \sum_{i=1}^{n} \frac{\text{actual [RAi] in solution}}{\text{LC50 for } \text{RA}_i}, \text{ where n = the number of RAs involved \& [RA] is the RA concentration}$$

In a simple case involving one resin acid species, a TU of 1 occurs when the RA concentration equals its LC50. If the TU is less than 1, then less than 50% of the fish would be expected to die (Sprague, 1970).

From the RA concentrations in the August 24-25 Fort Frances mill effluent (Table 5) and the LC50s of the individual RA's at a pH of 7.1 (Appendix M),

the TU =

$$\frac{\text{Dehydroabietic A. conc.}}{\text{Dehydroabietic A. LC50}} + \frac{\text{Abietic A. conc.}}{\text{Abietic A. LC50}} + \frac{\text{Neoabietic A. conc.}}{\text{Neoabietic A. LC50}}$$

$$\frac{\text{Isopimaric A. conc.}}{\text{Isopimaric A. LC50}} + \frac{\text{Levopimaric A. conc.}}{\text{Levopimaric A. LC50}} + \frac{\text{Pimaric A. conc.}}{\text{Pimaric A. LC50}} +$$

$$\frac{\text{Sandaracopimaric A. conc.}}{\text{Sandaracopimaric A. LC50}}$$

$$= \frac{<10}{1100} + \frac{472}{700} + \frac{130}{700} + \frac{106}{400} + \frac{695}{850} + \frac{67}{850} + \frac{56}{660} = 2.05, \text{ when } <10 \text{ is given a value of 5.}$$

Therefore, the TU of the full strength effluent is 2.05 if RAs account for all of its lethality, while a TU of 1.0 would occur at a concentration of 49%. An LC50 estimation of 49% is close to the actual LC50 measured in the laboratory bioassay (43%) and is just beyond its 95% confidence limits of 38-48% (Table 3). In the same manner, the August 25-26 Fort Frances mill effluent has a TU value of 2.65 and an estimate of its LC50 would be 38%. The actual LC50 in the bioassay of that sample was 31% with 95% confidence limits of 25-38%. From these data it would appear that RA's accounted for most, if not all of the effluent lethality and therefore should be considered as the primary lethal components in the waste for those particular cases.

Resin acids in the other two composite samples (days 3-4 and 4-5) do not account for all of the lethality observed in the lab bioassays of those samples. The OME Organic Contaminants lab which undertook all RA analyses have stated that RA values should be considered as minimum levels only (Y. Jones, pers. comm.). That qualification of resin acid analyses, when used in assessing the bioassay findings, suggests that the day 3-4 and 4-5 RA values for the effluent may be underestimations of true values. Hence, RA's may also be the primary lethal components in those two samples from the Fort Frances mill.

For the reference sample in Table 5, the TU concept would predict an LC50 at a 21% effluent concentration, on the basis of RA levels. The actual LC50 for that sample was 14% and confidence limits were 12.6-15.5%. These figures suggest that RAs account for much if not all of the acute lethality within that sample and lend further support to the suggestion that RAs are the major toxic component in this effluent.

Resin acid levels in the International Fall's mill effluent were basically non-existent with the exception of the day 3-4 sample. The TU value for RA's in that sample was 0.47 and as expected it was non-lethal. Likewise all of the other International Falls mill samples contained relatively low resin acid levels (Table 5) and were also non-lethal.

### iii) A Comparison of Rainbow Trout and Brown Sensitivity to the Boise Canada Pulp Mill Wastes

The use of rainbow trout in bioassays at temperatures above 20-21°C, especially under potentially reduced dissolved oxygen conditions, was not advisable. Therefore, brown trout were evaluated and used as a replacement for rainbow trout in the August field exposure, for browns are a sensitive fish species having a higher optimum temperature range than rainbow trout.

In 3 of 4 sets of bioassays to compare the sensitivity of the two species either to the Boise Cascade mill effluents or to lethal levels of a pulp mill contaminant (abietic acid), test results were virtually identical (Appendices B & C). In the fourth case, the Fort Frances mill effluent was approximately twice as lethal for rainbow trout as compared to the brown trout. There is no explanation for this difference other than to say that brown trout may be much less sensitive to the pulp mill wastes at less acutely lethal levels of the waste.

In regard to abietic acid toxicity, there was no significant difference ($p>0.05$) between the rainbow and brown trout bioassay results.

The use of an application factor to compare rainbow and brown trout sensitivities to the BKME plumes was not possible due to the fact that virtually no brown trout mortality occurred in the field exposure (i.e., LC50>100%). An application factor can only be applied when the LC50 for brown trout exposure at a river site is less than or equal to 100%. It is quite possible and highly probable that virtually all rainbow trout in a field exposure would have survived (result equivalent to brown trout findings). This conclusion is based on the May 14 and 18th, 1986 tests (Appendix B) and the abietic acid test results (Appendix C). Also, the highest concentration of effluent at an exposure site downstream of the Fort Frances mill was 6% during this study (Appendix H), while for the same period, an effluent concentration of at least 24% was required to produce an LC50 in lab bioassays of rainbow trout (Table 3). Therefore, just as was the case for the brown trout exposure, no LC50 would have occurred in the Rainy River for rainbow trout.

### (iv) A Comparison of Laboratory and Field Bioassay Results

Laboratory bioassays of the Boise Cascade Fort Frances mill effluent demonstrated fish lethality with LC50's ranging from 29-43% in four samples. The lowest concentration of effluent in those tests with no fish mortality, occurred in the 18% test solution.

The only mortality directly downstream of the Fort Frances mill was in the effluent upwelling from the diffuser discharge. A fathead minnow mortality level of 8% occurred in the upwelling during of 48-h exposure, while the maximum effluent concentration at that site was 6% (Appendix H). However, a bioassay result of less than 10% fish mortality is not considered a significant biological response (i.e. in laboratory bioassays, control mortality of 10% or less are not significant enough to invalidate the test result (Craig et al, 1983)). Therefore the lab bioassays which include no lethality at an 18% effluent concentration and field results of virtually no lethality at a 6% concentration, are considered to be consistent. In essence, the mill diffuser system produced a greater than 10 to 1 dilution of river water to effluent, by the time the effluent reached the river surface, which in turn all but eliminated acute lethality to fish in the effluent plume.

There was no rainbow trout lethality observed in four lab bioassays of the International Falls mill effluent collected daily during the study, and all brown trout sited in cages 15 and 65 m directly downstream of the International Falls diffuser port system survived the 96-h exposure.

### 2. Some Potential Sources of Dioxin and Furan Contamination in the Effluents

Certain forms of tetra chlorinated dibenzofuran ($T_4CDF$) are very toxic. The most lethal $T_4CDF$ congener, 2,3,7,8-TCDF, is considered to be half as toxic as the most lethal dioxin, 2,3,7,8-TCDD (Birmingham, et al, 1986). A level of 80 pg $T_4CDF/L$ was found in one sample of the Boise Cascade (Fort Frances) effluent (Table 15) along with the hepta and octa CDD and CDF contaminants in a second sample (Table 16). Rappe et al. (1978) have found levels of tetra, hepta and octa CDFs in two commercial chlorophenol (CP) products; 2,4,6-trichlorophenol and pentachlorophenol. If present in commercial CP products, polychlorinated dibenzofurans could also be produced in situations where certain chlorophenols are made as by-products of the kraft mill bleaching process.

The hepta and octa CDD's (dioxins), of which the latter was detected in both mill effluents (Table 16), may also be present due to CP's. One of the main routes for the formation of dioxins is by heating the various salts of chlorophenols (Buser, 1975). In technical grade pentachlorophenol marketed in Canada, octa CDDs and hepta CDDs were measured at levels of 120-650 and 35-280 µg/g, respectively (Environment Canada, 1985).

Another potential source of dioxins in the effluent may be the phenoxy acids (Table 13), and within that group of herbicides; 2,4,5-T is a known source of dioxins in other situations (Firestone et al., 1972; Elvidge, 1971). In 1985, we (the NW Region) investigated the use of 2,4,5-T in aerial spray programs with respect to the Rainy River. We determined that 2,4,5-T was last used in the mid-1970's as a mixture with 2,4-D by the Ministry of Natural Resources (MNR) in its conifer release aerial spray programs. Ontario Hydro also used the herbicide 2,4,5-T on a limited basis for maintaining power line right of ways. Since then, 2,4,5-T has been banned for use in Ontario. It is our view that the use of 2,4,5-T in Ontario was never a significant source of dioxins/furans to fish in the Rainy River.

Cochrane et al. (1981) have found di-, tri and tetra chlorinated dibenzodioxins in 2,4-D formulations, obtained from sources representative of those available in Canada. Therefore, certain dioxins found in sportfish from the Rainy River may be associated with aerial spraying of phenoxy acid herbicides in forest management programs or as residues on wood supplies processed in the mills. However, it is important to realize that although the very toxic 2,3,7,8-TCDD was found in the herbicide 2,4,5-T, which led to a ban of 2,4,5-T use in Canada, 2,3,7,8-TCDD was not detected in 2,4-D (Cochrane et al., 1981) and is not expected to be found therein due to differences in its manufacturing process (NRC, 1983).

As well as being formed as process by-products, the presence of dioxins and furans in the mill effluents may also be due to the use of commercial products in the mills which contain chlorophenols as their principal components, such as preservatives for wood processing materials (Jones, 1981). In fact, several sources of dioxins and/or furans may be present within the mills.

### 3. Chlorophenol Bioaccumulation by Fish

The uptake portion of the study demonstrated very limited bioconcentration of chlorophenols by fish even though chlorophenols were measured in water samples throughout much of the study area. The two main areas of the river at which elevated chlorophenol residues occurred in fish, were in the diffuser upwelling of the Fort Frances mill and 30 m downstream of the International Falls Municipal STP. The source of 2,4,6-trichlorophenol and pentachlorophenol bioconcentrated by fish at the upwelling site was the Fort Frances mill effluent. No chlorophenols were detected in fish at the control sites or at the next closest site downstream of the mill (250 m downstream at the tip of the hydro tower peninsula).

The International Falls STP was the probable source of pentachlorophenol downstream of the STP for none was detected in fish directly upstream and a transboundary effluent migration from Canadian sources would not have occurred within the necessary distances downstream of their discharges.

There was no 2,4,6-trichlorophenol detected in the International Falls STP effluent and no residues were detected in fish on the Canadian side of the river with the exception of the mill diffuser upwelling. Therefore, the probable source of 2,4,6-trichlorophenol traces in fish downstream of the International Falls mill is the mill effluent.

Two published reports relate body burdens of CPs in freshwater fish to lethal effects. Kobayashi and Kishino (1982) report that the incipient lethal level of PCP in goldfish (Carassius auratus) was 9200 ng PCP/g of body weight, and was independent of pH variations in the test water. In another paper, Spehar et al. (1985) found that PCP concentrations of 7500 μg/g were present in dead fathead minnows (Pimephales promelas). The highest concentration to cause no effect on egg hatchability, skeletal development of larval fish, survival and growth occurred with PCP body burdens of 3500 ng/g, accumulated over 32 days (Spehar et al., 1985).

The OME study took place over 5 days as compared to long-term studies in the literature of up to 160 days. However, maximum bioaccumulation factors (BCFs) in this study are equivalent to any cited in the literature for PCP. Spehar et al. (1985) demonstrated BCFs for PCP of up to 1066 over a 32-day period. Other BCFs found for PCP are 460 for rainbow trout (Salmo gairdneri) over 280 h (McKim et al., 1986), 240 for rainbow trout (Salmo gairdneri) over 115 days (Nimii and McFadden, 1982) and 770 for fathead minnows (Pimphales promelas) over 32 days (Veith et al., 1979). BCFs in the Rainy River study ranged up to 1125 for samples in which PCP was detected. Therefore, body burdens of PCP in fathead minnows and brown trout in this study are consistent with what would be expected over a longer-term study.

The PCP levels in fish of this study ranged from non-detectable to 60 ng/g, while Spehar et al. (1985) detected no effect levels in fathead minnows of 3500 ng/g. The no effect levels of 3500 ng/g were nearly sixty-fold greater than levels in fish exposed during this study. These results suggest no environmental effect of PCP on the Rainy River fishery under low flow (worst case) river conditions, especially considering that fish are generally the most sensitive biota to PCP (USEPA, 1987). In regard to PCP levels in water, the highest level in the river, 100 ng/L downstream of the Fort Frances STP (Tables 11 & 12), was one-fifth of the current Provincial Water Quality Objective of 500 ng/L for PCP (DeBarros, pers. comm.).

There is no literature available which relates body burdens of 2,4,6-TCP in fish to stress-related effects. The Provincial Water Quality Objective for trichlorophenols in surface waters is 18,000 ng/L (DeBarros, pers. comm.). All mill effluents, STP effluents and river surface waters met that objective during this study (Tables 8, 9, 11 and 12).

# CONCLUSIONS

1. The Boise Cascade (International Falls) mill effluent was found to be non-lethal, while the Fort Frances mill effluent was acutely lethal in each of four laboratory bioassays. Furthermore, in the latter case, the effluent did not meet the Ontario Government toxicity test requirement for pulp and paper mill wastes, of at least 50% rainbow trout survival in a 100% effluent concentration.

2. In the laboratory bioassays which were lethal, resin acids appeared to be the primary lethal component.

3. The effluent plume downstream of the International Falls mill was not acutely lethal to fish, and lethality downstream of the Fort Frances mill did not occur at significant levels relative to control mortality. Therefore, acute lethality to fish immediately downstream of both Boise Cascade pulp mills is not considered to be a problem under normal mill operations and low flow river conditions.

4. All chlorophenol levels in the Rainy River were below Provincial Water Quality Objectives for the protection of aquatic life.

5. The chlorophenol residues detected in fish under worst case (low flow) river conditions, were at concentrations of <110 ng/g. These low levels confirm that chlorophenol bioconcentration is not considered to be of a concern to the health of fish in the Rainy River.

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APPENDIX A: Test Fish Acclimation Data

| | Lakehead University | | OME Rexdale | Lakehead University | *In situ* Bioassay Rainy River |
|---|---|---|---|---|---|
| Test Dates | 14/5/86 | 29/5/86 | 12/5/86 | 25/8/86 | 24/8/86 |
| Fish Species #1 | Rainbow Trout | Rainbow Trout | Rainbow Trout | Rainbow Trout | Brown Trout |
| Source of Fish | Rainbow Spring Trout Farm, Thamesford | | Rainbow Springs Trout Farm | Rainbow Springs Trout Farm | MNR Codrington Hatchery |
| Age | Young-of-the-Year | | Young-of-the-Year | Young-of-the-Year | Young-of-the-Year |
| Weight | 0.8 ± 0.3 g | 0.6 ± 0.2 g | 1.2 ± 0.3 g | 1.1 ± 0.3 g | 3.7 ± 0.7 g |
| Length | 4.0 ± 0.3 cm | 3.6 ± 0.3 cm | 4.5 ± 0.5 cm | 4.2 ± 0.3 | - |
| Acclimation Period | 27 days | 14 days | >10 days | 21 days | 39 days |
| Photoperiod | 14:30 h Light | 15.15 h Light | 15 h Light | 14:15 h Light | 14:15 h Light |
| Fish Species #2 | Brown Trout | Brown Trout | Brown Trout | | Fathead Minnows |
| Source of Fish | Sir Sandford Fleming College, Lindsay | | SSF College | | OME Rexdale Lab. |
| Age | Young-of-the-Year | | Young-of-the-Year | | 5 months old |
| Weight | 2.1 ± 0.9 g | 1.3 ± 0.7 g | 1.0 ± 0.2 g | | 1.8 ± 0.2 g |
| Length | 5.1 ± 0.7 cm | 4.4 ± 0.6 cm | 3.8 ± 0.2 g | | - |
| Acclimation Period | 20 days | 36 days | >30 days | | 39 days |
| Photoperiod | 14:30 Light | 15:15 Light | 15 h Light | | 14:15 h Light |

## APPENDIX B: A Comparison of the Bioassay Results for the Boise Cascade Effluents Using Rainbow and Brown Trout During May, 1986

| Mill Location | Test Species | Test Date | Code Test No. | LC50 (%) | 95% Confidence Levels |
|---|---|---|---|---|---|
| Fort Frances | Rainbow Trout | 14/05/86 | 014 (F) | 11.2 | 10.0 - 12.5 |
| | Brown Trout | 14/05/86 | 015 (F) - A | <10.0 | - |
| | | 18/05/86 | 015 (F) - B | 10.0 | UTC |
| | Rainbow Trout | 29/05/86 | 024 (F) | 16.5 | 14.2 - 19.1 |
| | Brown Trout | 29/05/86 | 025 (F) | 39.5 | 30.1 - 52.8 |
| International Falls | Rainbow Trout | 14/05/86 | 016 (F) | >100 | - |
| | Brown Trout | 14/05/86 | 017 (F) | >100 | - |

## APPENDIX C: A Comparison of the Bioassay Results for Abietic Acid Using Rainbow and Brown Trout

| Test Species | Test Date | Code Test No. | LC50 (mg/L) | 95% Confidence Levels |
|---|---|---|---|---|
| Brown Trout | 12/05/86 | S-18 | 6.66 | 5.78 - 7.66 |
| Brown Trout | 12/05/86 | S-19 | 6.00 | 5.23 - 6.90 |
| Brown Trout | 12/05/86 | S-20 | 5.53 | 4.93 - 6.21 |
| Rainbow Trout | 12/05/86 | S-21 | 5.28 | 4.85 - 5.76 |
| Rainbow Trout | 12/05/86 | S-22 | 5.28 | 4.85 - 5.76 |
| Rainbow Trout | 12/05/86 | S-23 | 5.79 | 5.08 - 6.61 |

Note: UTC: indicates unable to calculate.

## APPENDIX D: Reactive Phenolics in the Boise Cascade (Fort Frances & International Falls) Diffuser Effluents, August 24-28, 1986 (Study Days 1-5, respectively).

| Study Days | Sample Type | Phenolic Concentrations (µg/L) for<br>Pithers Pt. (Control) | <br>B.C. Fort Frances | <br>B.C. Internat'l Falls |
|---|---|---|---|---|
| 1 | grab | 1.4 | - | - |
| 1-2 | 24 h comp. | - | 3.0 | - |
| 1-2 | 15 h comp. | - | - | 4.2 |
| 2 | grab | 1.8 | - | - |
| 2-3 | 24 h comp. | - | 225 | - |
| 3 | grab | 3.6 | - | 5.8 |
| 3-4 | 24 h comp. | - | 156 | 7.6 |
| 4 | grab | 1.4 | - | - |
| 4-5 | 24 h comp. | - | 130 | - |
| 5 | grab | 2.0 | - | 8.0 |
| Average<br>Range | | 2.0<br>(1.4 - 3.6) | 129<br>(3-225) | 6.4<br>(4.2 - 8.0) |

NOTE: Analyses undertaken using the 4-aminoantipyrene colourmetric Method A.

## APPENDIX E: Resin and Fatty Acid Concentrations in the Rainy River at Cage Sites Downstream of the Boise Cascade Fort Frances & International Falls Mills, August 24-26, 1986 (Exposure Days 1-3 for each of the exposures).

| Study Day/ Site | Resin & Fatty Acid Levels (µg/L) | | | | |
|---|---|---|---|---|---|
| | Palmitic | Linoleic | Monochloro-Abietic | Levo-Pimaric | All Other R & FA |
| Day 1 | | | | | |
| All Sites[1] | nd | nd | nd | nd | nd |
| Day 2[1] | | | | | |
| Site A | 26 | 23 | nd | nd | nd |
| Site E | 34 | 24 | nd | nd | nd |
| Day 3 | | | | | |
| Site 4 | nd | nd | 20 | nd | nd |
| Site 6 | nd | nd | 54 | nd | nd |
| Site 8 | nd | nd | 18 | nd | nd |
| Site C | nd | nd | 80 | nd | nd |
| Day 4 | | | | | |
| Site 4 only[2] | nd | nd | nd | nd | nd |
| Day 5 | | | | | |
| Site 4 only[2] | nd | nd | nd | 21 | nd |

NOTE: [1] All sites sampled except site 4.
Site 4 was sampled on day 3, 4 & 5 only.
[2] Only site 4 was sampled.
Only sites with detectable levels of R & FA are listed in the above table.
Detection levels were 10 µg/L.

## APPENDIX F: Dissolved Oxygen Levels on the Canadian Side of the Rainy River Up and Downstream of the Boise Cascade (Fort Frances) Mill Diffuser from August 25-27, 1986 (Study Days 2-4, respectively).

| No. | Site Description | Dissolved Oxygen (mg/L) on Study Days | | |
|---|---|---|---|---|
| | | 2 | 3 | 4 |
| C-1 | Control-Island NW of Gash Point | 8.8 | - | - |
| C-2 | Control - Pithers Point | 9.0 | 9.1 | 9.5 |
| C-3 | Control - Log Boom 300 m Upstream of International Bridge | 9.1 | 9.2 | 9.8 |
| 4 | Mill Diffuser Plume Upwelling | - | 8.5 | 8.9 |
| 5 | Hydro Tower Peninsula | 8.4 | 8.5 | 9.1 |
| 6 | Adjacent to 1st Set of Islands Downstream of Mill | 8.2 | 8.8 | 8.7 |
| 7 | Fort Frances STP - 30m Downstream of Diffuser | 8.5 | 8.4 | 8.7 |
| 8 | Canadian Greenhouses - 100 m Downstream | 8.4 | 8.2 | 8.6 |
| 9 | First Major Bend Downstream of the Mill | 8.4 | 8.2 | 8.6 |
| 10 | Canadian Side Opposite American Golf Course | 8.0 | 8.2 | 8.7 |

## APPENDIX G: Dissolved Oxygen Levels on the American Side of the Rainy River Downstream of the Boise Cascade (International Falls) Mill Diffuser, August 25-27, 1986 (Study Days 2-4, respectively).

| No. | Site Description | Dissolved Oxygen (mg/L) on Study Days 2 | 3 | 4 |
|---|---|---|---|---|
| A | 15m Downstream of Mill's 6th Diffuser Port | 7.8 | 8.3 | 8.6 |
| B | 65m Downstream of Mill Diffuser | 7.6 | 8.4 | 8.6 |
| C | Adjacent to 1st Set of Islands Downstream of Mill | 8.2 | 8.4 | 8.3 |
| D | International Falls STP - 30m Downstream of Diffuser | 8.4 | 8.4 | 8.3 |
| E | Shore Opposite Canadian Greenhouses | 8.2 | 8.3 | 8.4 |
| F | First Major Bend Downstream of Mill | - | 8.3 | 8.2 |
| G | Adjacent to Golf Course | 8.2 | 8.2 | 8.7 |

## APPENDIX H: Conductivity Levels (µmhos/cm) and Calculated Mill Effluent Concentrations (%) on the Canadian Side of the Rainy River Downstream of Boise Cascade (Fort Frances) Mill Diffuser, August 25-28, 1986 (Study Days 2-5, respectively).

| No. | Site Description | Conductivity & Related Effluent Concentrations (in brackets)[1] on Study Days 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| 4 | Mill Diffuser Plume Upwelling | - | 115 (6%) | 70 (3%) | 120 (6%) |
| 5 | Hydro Tower Peninsula | 50 (1%) | 45 (1%) | 45 (1%) | 60 (1%) |
| 6 | Adjacent to 1st Set of Island Downstream of Mill | 50 (1%) | 50 (1%) | 40 (1%) | 60 (1%) |
| 7 | Fort Frances STP-30 m Downstream of Diffuser | 45 (1%) | 45 (1%) | 50 (1%) | 55 (1%) |
|  | Other Pertinent Sites |  |  |  |  |
| C-3 | Control - Log Boom 300 m Upstream of International Bridge | 35 | 35 | 35 | 40 |
| FSE | Diffuser Effluent (Full Strength) | 1399 | 1396 | 1420 | 1386 |

[1] Effluent Concentrations based on Relative Conductivity ($C_R$) using the Formula $C_R = \frac{Cr - Crc}{Ce - Crc}$

where Cr = conductivity at a specific test site,
Crc = conductivity at a river control site (C-3)
and Ce = conductivity of the full strength effluent sample (FSE listed above).

NOTE: All values obtained from grab samples.

## APPENDIX I: Conductivity Levels (µmhos/cm) and Calculated Mill Effluent Concentrations (%) on the American Side of the Rainy River Downstream of Boise Cascade (International Falls) Mill Diffuser, August 25-28, 1986 (Study Days 2-5, respectively).

| | | Conductivity & Related Effluent Concentrations (in brackets)[1] on Study Days | | | |
|---|---|---|---|---|---|
| No. | Site Description | 2 | 3 | 4 | 5 |
| A | 15m Downstream of the 6th Diffuser Port | 90 (8%) | 110 (12%) | 70 (5%) | 160 (14%) |
| B | 65m Downstream of Mill Diffuser | 95 (9%) | 85 (8%) | 70 (5%) | 135 (11%) |
| C | Adjacent to 1st Set of Islands Downstream of Mill | 90 (8%) | 85 (8%) | 85 (8%) | 115 (9%) |
| D | International Falls - STP 30m Downstream of Diffuser | 70 (5%) | 70 (6%) | 60 (4%) | 100 (7%) |
| E | Shore Opposite Canadian Greenhouses | 75 (6%) | 70 (6%) | 70 (5%) | 95 (7%) |
| F | First Major Bend Downstream of the Mill | 75 (6%) | 75 (6%) | 65 (5%) | 95 (7%) |
| G | Adjacent to Golf Course | 60 (4%) | 55 (3%) | 55 (3%) | 60 (2%) |
| | Other Pertinent Sites | | | | |
| C-3 | Control - at Log Boom 300m Upstream of International Bridge | 35 | 35 | 35 | 40 |
| FSE | Diffuser Effluent (Full Strength) | 706 | 672 | 695 | 872 |

[1] Effluent Concentrations based on Relative Conductivity ($C_R$) using the Formula $C_R = \frac{Cr - Crc}{Ce - Crc}$

where Cr = conductivity at a specific test site
Crc = conductivity at a river control site (C-3)
and Ce = conductivity of the full strength effluent sample (FSE listed above).

NOTE: All values obtained from grab samples.

APPENDIX J: Organochlorine Concentrations in the Boise Cascade (Fort Francis & International Falls) Diffuser Effluents, August 24-28 (Study Days 1-5, respectively).

| Organochlorine Species | Organochlorine Concentrations (ng/L) in the Boise Cascade (Fort Frances) Effluent on Study Days | | | | Organochlorine Concentrations (ng/L) in the Boise Cascade (International Falls) Effluent on Study Days | | | |
|---|---|---|---|---|---|---|---|---|
| | 1-2 | 2-3 | 3-4 | 4-5 | 1-2 | 2-3 | 3-4 | 4-5 |
| Hexachlorobenzene | nd | 13 | nd | 3 | nd | nd | 38 | 50 |
| Heptachlor | nd | 2 | nd | 17 | nd | nd | nd | nd |
| A-BHC Hexachlorocyclohex | nd | nd | nd | nd | nd | 1 | nd | nd |
| B-BHC Hexachlorocyclohex | 42 | nd | nd | 36 | 27 | nd | nd | nd |
| A-Chlordane | nd | nd | nd | nd | nd | 2 | nd | 5 |
| G-Chlordane | 16 | nd | nd | nd | nd | nd | nd | nd |
| OP-DDT | nd | nd | 30 | nd | nd | nd | nd | 35 |
| PP-DDD | nd | nd | nd | nd | nd | nd | 10 | nd |
| PP-DDT | nd | nd | nd | nd | nd | 10 | 40 | 30 |
| DMDT Methoxychlor | nd | nd | nd | nd | nd | 160 | 120 | 55 |
| Heptachlorepoxide | nd | nd | nd | 33 | nd | nd | nd | nd |
| Endosulfan I | nd | nd | nd | 14 | nd | nd | nd | nd |
| Endosulfan sulphate | nd | 60 | 48 | nd | nd | 160 | 68 | 48 |

NOTE: nd - indicates not detected

| Organochlorine Analyses Undertaken | Detection Levels (ng/L) | Organochlorine Analyses Undertaken | Detection Levels (ng/L) |
|---|---|---|---|
| PCB | 20 | Oxychlordane | 2 |
| Hexachlorobenzene | 1 | OP-DDT | 5 |
| Heptachlor | 1 | PP-DDD | 5 |
| Aldrin | 1 | PP-DDT | 5 |
| PP-DDE | 1 | DMDT Methoxychlor | 5 |
| Mirex | 5 | Heptachlorepoxide | 2 |
| A-BHC | 1 | Endosulfan I | 2 |
| B-BHC | 1 | Dieldrin | 4 |
| G-BHC | 1 | Endrin | 4 |
| A-Chlordane | 2 | Endosulfan II | 4 |
| G-Chlordane | 2 | Endosulfan Sulphate | 4 |

## APPENDIX K: Boise Cascade (Fort Frances) Mill Operations from August 24-30, 1986.

| | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
|---|---|---|---|---|---|---|---|
| Flow to River (MGDUS)[1] | 20.06 | 20.35 | 20.71 | 20.34 | 19.82 | 19.58 | 19.75 |
| pH | 6.9 | 7.0 | 7.0 | 6.9 | 7.0 | 7.0 | 6.9 |
| TSS to River (lbs/D x 1000) | 18.6 | 21.2 | 22.8 | 18.0 | 14.0 | 15.4 | 18.2 |
| BOD to River (lbs/D x 1000) | 18.1 | 21.5 | 23.4 | 20.5 | 18.0 | 19.4 | 17.8 |
| Pulp Production (ADTPD)[2] | | | | | | | |
| - kraft | 481.5 | 541.8 | 577.1 | 621.0 | 580.5 | 561.6 | 573.3 |
| - groundwood | 430.2 | 405.9 | 387.0 | 516.6 | 399.6 | 508.5 | 454.5 |
| Paper Production (ADTPD) | 741.3 | 585.1 | 556.7 | 697.1 | 591.2 | 690.6 | 796.1 |
| Wood Debarked | | | | | | | |
| - dry (ADTPD) | 488 | 427 | 407 | 544 | 420 | 471 | 479 |
| - wet (TPD) | 2358 | - | 542 | 861 | 870 | 274 | - |
| Digester Blows (#) | 29 | 32 | 28 | 33 | 32 | 31 | 33 |

NOTE: No major spills reported - $BOD_5$ loading from kraft mill to treatment facility increased near end of week due to shutdown preparations.

[1] MGDUS: Millions of U.S. gallons per day
[2] ADTPD: Air-dried tons per day

## APPENDIX L: Boise Cascade (International Falls) Mill Operations from August 24-30, 1986.

| | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
|---|---|---|---|---|---|---|---|
| Flow to River (MGDUS)[1] | 35.39 | 36.34 | 34.27 | 32.431 | 34.08 | 34.09 | 35.52 |
| pH to River | 7.1 | 7.2 | 7.2 | 7.5 | 7.0 | 7.2 | 7.1 |
| TSS to River (lbs/D) | 1760 | 3640 | 6140 | 3780 | 5120 | 15900 | 8880 |
| BOD to River (lbs/D) | 885 | 606 | 857 | 1082 | 853 | 5402 | 2370 |
| Pulp Production (estimated ADTPD)[2] | 479 | 456 | 228 | 415 | 459 | 459 | 291 |
| Paper Production (gross TPD) | 1262 | 1124 | 1252 | 1195 | 1348 | 1310 | 1265 |
| Wood Usage (estimated ADTPD) | 812 | 773 | 386 | 703 | 778 | 778 | 493 |
| Digester Blows (#) | 39 | 37 | 17 | 35 | 39 | 37 | 36 |
| Spills/Plant Upsets | (sewered 60 tons of bleached SW[3] over 25th and 26th) | | | | | | |

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[1] MGDUS: Millions of U.S. gallons per day

[2] ADTPD: Air-dried tons per day

[3] SW: Sour water

## APPENDIX M: Acute Toxicity of Resin Acids to Fish
All Bioassays Static Unless Indicated Otherwise

| Compound | Species[a] | 96 h LC50 (mg/L) | Test Conditions | Source |
|---|---|---|---|---|
| Dehydroabietic Acid | Rainbow Trout | 1.1 | pH 7.0, hardness 47.0 mg/L | Davis and Hoos 1975 |
| Abietic Acid | Rainbow Trout | 0.7 | pH 7.0 + 0.1 | Leach and Thakore 1976 |
| Neoabietic Acid | Rainbow Trout | 0.7 |  | Leach and Chung 1980 (from McLeay 1986) |
| Isopimaric Acid | Rainbow Trout | 0.4 | pH 7.0 + 0.1 | Leach and Thakore 1976 |
|  | Coho Salmon | 0.22 | semi-static, pH 7.0 | Leach and Thakore 1977 |
| Levopimaric Acid | Rainbow Trout | 0.7-1.0 | pH 6.4, hardness 4.8 mg/L | Chung et al. 1979 |
| Pimaric Acid | Rainbow Trout | 0.7-1.0 | pH 7.0 + 0.1 | Leach and Thakore 1976 |
| *Sandaracopimaric Acid | Coho Salmon | 0.36* | semi-static, pH 7.0 | Leach and Thakore 1977 |

* The LC50 value in the TU calculations with Sandaracopimaric Acid is approximately twice the value cited in this table based on the difference in results for static versus semi-static test with rainbow trout versus coho salmon for the two values of Isopimaric Acid in this table.

Note: (1) The table is taken from Taylor et al. (1988).
(2) The LC50s for abietic acid in the comparison of rainbow trout and brown trout sensitivity to abietic acid (Appendix C) were much higher due to differences in pH levels of the test solutions relative to levels in Appendix M bioassay results.

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